

3191

IQBAL LIBRARY  
THE UNIVERSITY OF KASHMIR

Call No....

ACC. No 10758

25 MAR 1996

12/13/96

27 AUG 2005

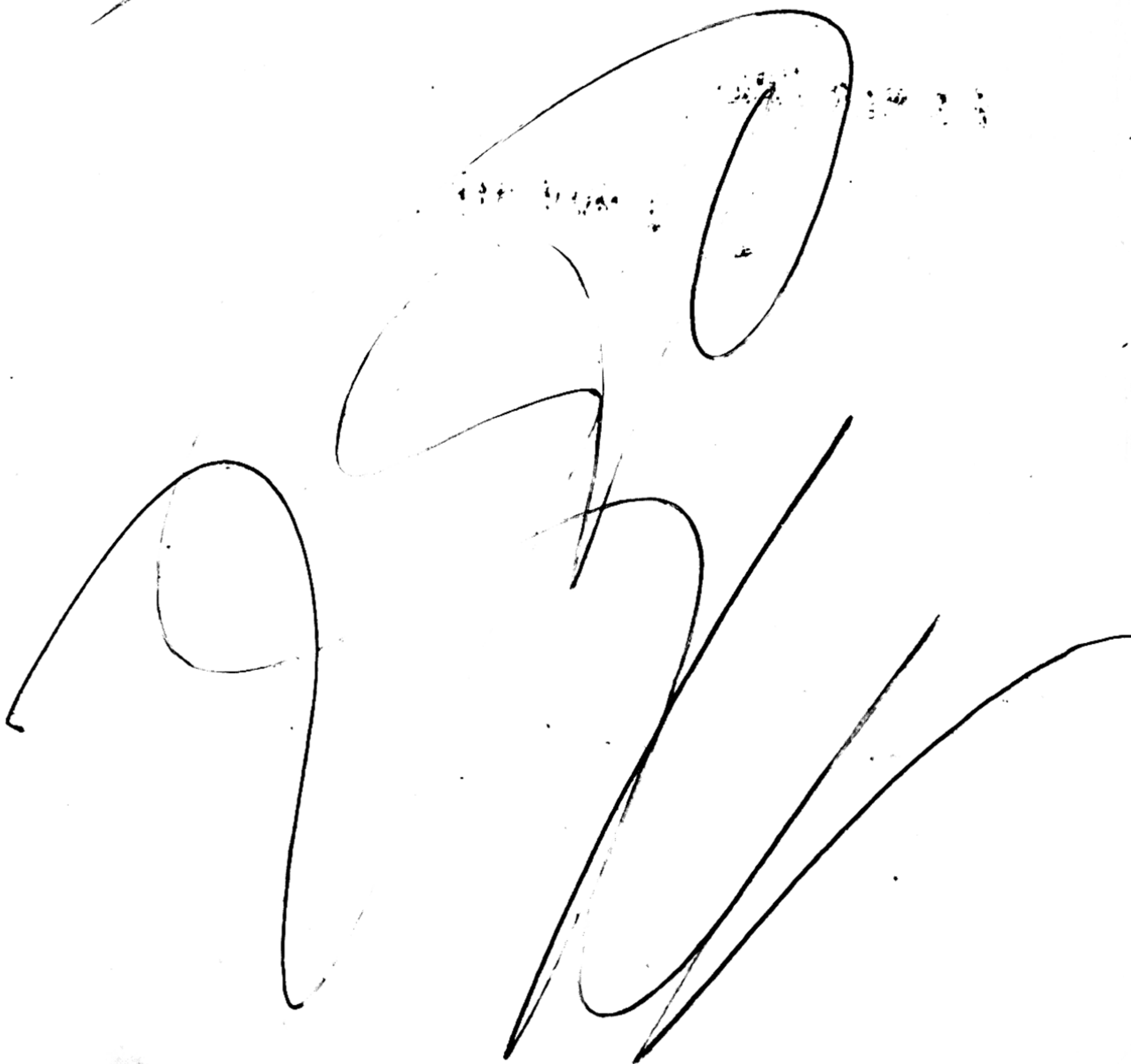
59

Overdue charges will be levied under rules for each day if the book is kept beyond the date stamed above.



land

220







# **ELEMENTARY QUANTITATIVE ANALYSIS**

**BY CARL J. ENGELDER**

**FUNDAMENTALS OF SEMI-MICRO  
QUALITATIVE ANALYSIS**

Cloth; 6 by 9¼; 389 pages.

**A TEXTBOOK OF ELEMENTARY  
QUALITATIVE ANALYSIS**

Third Edition. Cloth; 6 by 9¼; 344  
pages.

**LABORATORY RECORD BOOK OF  
QUALITATIVE ANALYSIS**

Second Edition. Paper; 6 by 9¼; 91  
pages.

**CALCULATIONS OF QUALITATIVE  
ANALYSIS**

Second Edition. Cloth; 6 by 9¼; 174  
pages.

**A TEXTBOOK OF ELEMENTARY  
QUANTITATIVE ANALYSIS**

Third Edition. Cloth; 6 by 9¼; 283  
pages.

**LABORATORY RECORD BOOK OF  
QUANTITATIVE ANALYSIS**

Second Edition. Tables. Paper; 6 by  
9¼; 96 pages.

**CALCULATIONS OF QUANTITATIVE  
ANALYSIS**

Cloth; 6 by 9¼; 174 pages.

**A LABORATORY MANUAL OF GAS, OIL  
AND FUEL ANALYSIS**

Cloth; 6 by 9¼; 236 pages.

---

**BY CARL J. ENGELDER  
TOBIAS H. DUNKELBERGER  
AND WILLIAM J. SCHILLER**

**SEMI-MICRO QUALITATIVE ANALYSIS**

Second Edition. Cloth; 6 by 9¼; 305  
pages.

---

**PUBLISHED BY  
JOHN WILEY & SONS, INC.  
NEW YORK**

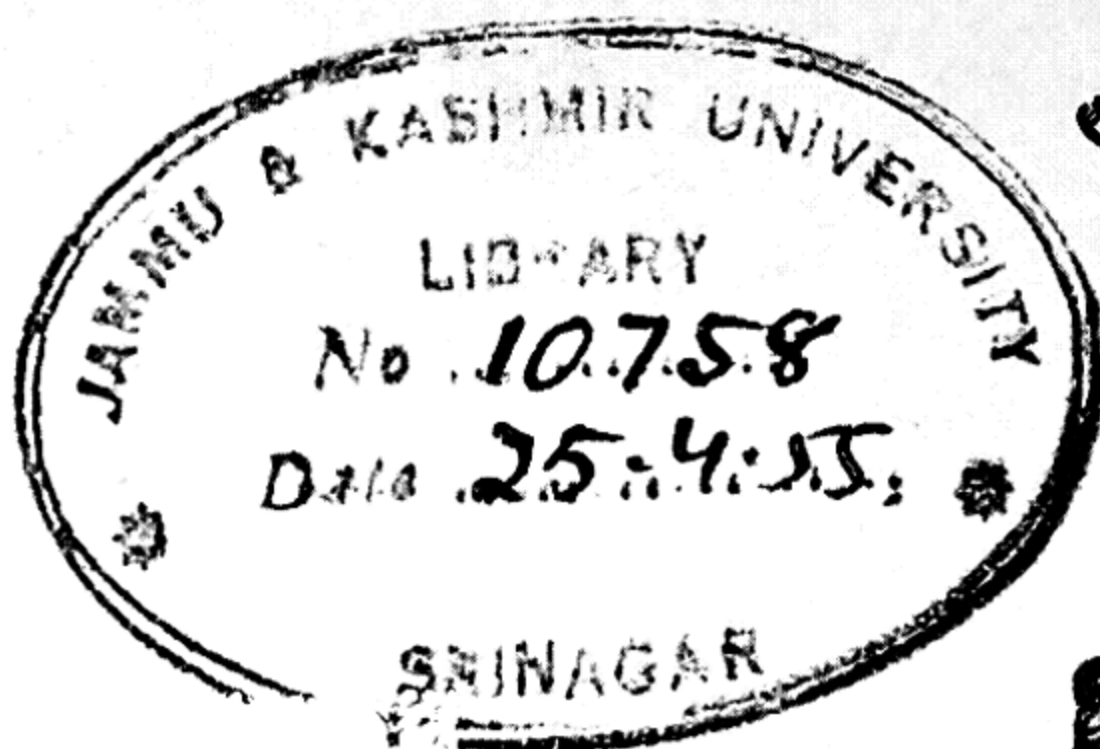
*A Textbook of*  
**ELEMENTARY  
QUANTITATIVE  
ANALYSIS**

BY  
**CARL J. ENGELDER, PH.D.**  
PROFESSOR OF ANALYTICAL CHEMISTRY  
UNIVERSITY OF PITTSBURGH

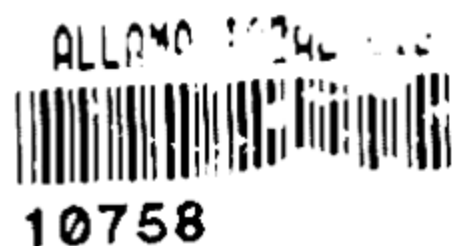
**THIRD EDITION**

**NEW YORK · JOHN WILEY & SONS, INC.**  
**LONDON · CHAPMAN & HALL, LIMITED**





ST 01  
R 61



COPYRIGHT, 1929, 1936, 1943

BY

CARL J. ENGELDER

*All Rights Reserved*

*This book or any part thereof must not  
be reproduced in any form without  
the written permission of the publisher.*

THIRD EDITION

*Fifth Printing, September, 1947*

✓ 545  
En 43 T

*revised*

PRINTED IN THE UNITED STATES OF AMERICA

## PREFACE

This book of Elementary Quantitative Analysis appeared first in 1929. It was revised in 1936, the most important change being the reversal of the gravimetric with the volumetric technique. Now, again, another revision has been made, the third edition being herewith presented.

Attention is called to the more noteworthy alterations involved in this revision. The most important shift has been to place volumetric precipitation methods directly preceding gravimetric precipitation methods; this has the advantage of not only placing both types of precipitation methods close together but of also introducing the concepts of equivalent weights and normal solution with acids and bases. The volumetric chloride determination is an added procedure in this revision.

In general, much of the text material has been rewritten and brought up to date by the adoption of better indicators, less emphasis on titers, etc. Procedures for limestone and brass have been merely outlined. A chapter on systematic quantitative analysis has been added, which incorporates two useful tabulations.

Problem work has been enlarged and arranged to cover fifteen weekly assignments, each problem set containing ten problems with answers and ten without answers. This should greatly facilitate the work of instruction in stoichiometry.

Acknowledgment is made to Lundell, Hoffmann and Bright, authors of *Outlines of Methods of Chemical Analysis*, for use of the table of electrode potentials and for tabulations upon which "The Distribution of the Elements in the General Procedure" and "Summary of Analytical Methods" were based.

CARL J. ENGELDER

*University of Pittsburgh*  
*January, 1943*





# CONTENTS

## *PART I*

### FUNDAMENTAL PRINCIPLES OF QUANTITATIVE ANALYSIS

CHAPTER	PAGE
I. GENERAL CONSIDERATIONS OF QUANTITATIVE ANALYSIS. . . .	1
The Scope of Quantitative Analysis. The Theoretical Basis of Quantitative Analysis. General Operations in Preparing Samples for Analysis. Errors and Precision of Quantitative Methods. Mathematical Operations. The Analytical Balance. Reagents.	

## *PART II*

### VOLUMETRIC ANALYSIS

II. THE THEORY, TECHNIQUE AND CALCULATIONS OF VOLUMETRIC ANALYSIS. . . . .	29
The Theory of Volumetric Analysis. Volumetric Apparatus and Technique. The Calculations of Volumetric Analysis.	
III. NEUTRALIZATION METHODS. . . . .	45
General Laboratory Instructions. General Considerations of Acidimetry and Alkalimetry. Determinations of Alkalinity and Acidity. Stoichiometric Calculations of Neutralization. The Theory of Neutralization.	
IV. OXIDATION AND REDUCTION METHODS. . . . .	99
General Considerations. Representative Oxidation-Reduction Procedures: A, Dichromate Methods; B, Permanganate Methods; C, Ceric Sulfate Methods; D, Iodine Methods.	
V. VOLUMETRIC PRECIPITATION METHODS. . . . .	160
Theory of Volumetric Precipitation.	

## PART III

## GRAVIMETRIC ANALYSIS

CHAPTER	PAGE
VI. THE THEORY, TECHNIQUE AND CALCULATIONS OF GRAVIMETRIC PRECIPITATION METHODS.....	169
Fundamental Requirements of Gravimetric Precipitation Methods. The Technique of Gravimetric Analysis. The Calculations of Gravimetric Analysis.	
VII. REPRESENTATIVE GRAVIMETRIC PRECIPITATION PROCEDURES	190
The Precipitation of Halides. The Precipitation of Hydroxides. The Precipitation of Sulfates. The Precipitation of Oxalates. The Precipitation of Phosphates. Calculations of Factor Weight Samples.	

## PART IV

## SYSTEMATIC QUANTITATIVE ANALYSIS

VIII. SYSTEMATIC ANALYSIS.....	213
Evolution Methods. Descriptive Outline of Limestone Analysis. Descriptive Outline of the Analysis of Brass. Calculations of Indirect Analysis. Summary of Analytical Methods.	

## APPENDIX

<i>The Literature of Analytical Chemistry.....</i>	241
<i>The Plan of the Course—Suggestions to the Instructor.....</i>	243
<i>Reagents and Supplies.....</i>	245
<i>Tables.....</i>	248
<i>Index.....</i>	281



*PART I*

*FUNDAMENTAL PRINCIPLES OF  
QUANTITATIVE ANALYSIS*

CHAPTER I

GENERAL CONSIDERATIONS OF QUANTITATIVE  
ANALYSIS

Chemistry became an exact science when quantitative methods of experimentation were introduced. The progress of modern chemistry is dependent upon exact quantitative measurements and rests upon the foundation of quantitative analysis first laid down by Lavoisier, Berzelius, Stas and others. The composition of matter and its transformations are determined by precise analysis. Back of the discovery of a new element, the synthesis of a new compound, the perfection of a new industrial process lies the story of careful, painstaking chemical analysis. Synthesis and analysis must go hand in hand in the advancement of chemical science.

In practically every field of human activity, chemistry, of which quantitative analysis is a fundamental and essential part, plays an important role. The application of chemistry to all phases of industry, to our well-being and to our everyday needs involves the work of the analyst. Much of the advance in medical science is the result of a careful chemical investigation of the factors concerned. The control of chemical manufacturing processes is directly dependent upon the analysis of the raw materials, often the intermediate products and usually the finished product. A research problem cannot be successfully pursued without a careful check by analysis at each step. A newly synthesized compound must be analyzed before its composition is definitely known. Even the determination of atomic weights depends upon the most precise quantitative methods of analysis. The influence of chemistry on our health, our happiness and our material advancement needs no emphasis.

The student who undertakes the study of quantitative analysis as part of his preparation for the profession of medicine, dentistry, pharmacy, engineering, mining, chemistry or the natural sciences cannot help

finding an enthusiastic appeal in the subject. Its application to his chosen profession is direct and fundamental. Through the training it offers in sound, logical reasoning, his chemical ideas are placed on a more secure and definite basis and his knowledge of chemical principles and relationships is enhanced. His training in the careful, exact manipulations of quantitative technique will always be of considerable value to him.

**Hints to Students.** The beginner's success in quantitative analysis depends largely on his approach to the subject and the attitude he maintains throughout the course. Too frequently at the outset, beginners have mistaken ideas that the subject is beyond their ability, that they cannot master the technique, that the calculations will prove too difficult. These ideas are unfounded and are quickly dispelled by the conscientious student who by diligent study keeps abreast of the laboratory and classroom assignments. A few students, on the other hand, do not give the subject the serious thought and best effort it deserves and soon find themselves hopelessly submerged. The student's efforts should be directed toward a clear understanding of the principles involved, the development of a reasonable dexterity in manipulation and a satisfactory facility in solving problems which express quantitative relationships.

Quantitative analysis imposes a severe discipline, and discouragements are apt to arise. The beginner must remember, however, that accidents sometimes occur in the best conducted experiments and ruin the analysis, and that perfect checks cannot always be hoped for in all determinations. Self-confidence and reliance in his own results are effective cures for discouragements. Confidence can be developed only by patient and persistent efforts to acquire the necessary skill in technique. When confidence in a determination is lost through the introduction of an error which is known to affect seriously the accuracy of the result, the analysis had better be abandoned and a fresh start made.

Absolute honesty is demanded of the analyst. The temptation to falsify results or to use the results of others must be resolutely resisted. No matter how discordant the results of an analysis are they should nevertheless be reported. Although closely agreeing results indicate, as a rule, reliable accuracy and reflect good ability in technique, they do not necessarily imply correct results because a similar large error may have been introduced in each determination. The habit of recording all data and calculations *in ink*, in a bound notebook is a good safeguard against any tendency deliberately to forge the results.

A laboratory notebook must be kept into which all observations, data and calculations are entered.\* Data such as the date, all weighings,

\* The author has prepared a *Laboratory Record Book of Quantitative Analysis*, published by John Wiley & Sons, Inc., New York.



buret readings and other observations should be recorded on the right-hand page and all calculations made on the left-hand page. The habit of recording data and making calculations on loose scraps of paper cannot be tolerated. Valuable data are sometimes lost in this way, errors are made in transcribing and, above all, the reliability of the results may be questioned. A neat, well-kept notebook reflects the owner's care and maintains his self-confidence. Writing should be done in ink and no erasures should be made; necessary corrections should be made without destroying the original entries.

Results, usually computed as percentages, are to be reported on forms supplied by the instructor; samples are shown in the Appendix. The procedures in this book call for making all determinations in triplicate, so that if one determination is ruined or the result lacks satisfactory agreement, at least two other results can be considered. Whether all determinations should be made in duplicate or in triplicate is left to the discretion of the instructor. The results will be judged by their deviation from the true composition of the sample.

To make intelligent progress the student must know what he is doing. He must thoroughly understand the principle involved and the reason for each step. This means that the student must study the procedure before he comes to the laboratory, so that valuable time is not wasted during the laboratory period and blunders may be avoided. Common sense must be used and the work must be carefully planned in order to make the best possible use of time. In general, two different sets of determinations should be in progress at the same time so that the time consumed in filtering, igniting and other operations may be effectively utilized otherwise.

## THE SCOPE OF QUANTITATIVE ANALYSIS

A quantitative analysis is made for the purpose of finding out *how much* of a given constituent is contained in the material under investigation. Before quantitative methods can be applied, it must be known *what* constituents are present; that is, a qualitative analysis of the material must first be made. Quantitative analysis, reaching out as it does into so many varied fields, uses methods which differ a great deal in principle and technique, depending upon the character of the material to be analyzed. The subject thus divides itself into many branches, the important divisions of which are: Inorganic and Organic Analysis; Food, Water and Sanitary Analysis; Gas, Oil and Fuel Analysis; Metallurgical Analysis; Assaying and Ore Analysis; Electrochemical Analysis; Microchemical Analysis; and many other specialized branches. The

methods taken up in this book are mainly those dealing with the determination of inorganic materials.

**Classification of Methods Based on Technique.** Quantitative methods differ much in the kind of technique employed. The following is a classification of methods based on the principal modes of procedure:

1. Volumetric methods.
2. Gravimetric methods.
3. Colorimetric methods.
4. Gas analytical methods.

Volumetric methods of analysis are the so-called titration methods, in which the amount of the desired constituent is determined by allowing the sample to react with a measured volume of reagent. Included under this heading are: (1) neutralization methods; (2) oxidation and reduction methods; and (3) volumetric precipitation methods. Included under this head are the potentiometric titration methods. Volumetric methods are taken up in Part II.

Gravimetric methods include those determinations: (1) in which the desired constituent is obtained as a precipitate by use of a chemical precipitating agent, the precipitate so obtained being purified and weighed (chemical precipitation methods); (2) in which the constituent is deposited by means of the electric current (electrolytic precipitation methods); and (3) in which a volatile constituent is driven from the sample (evolution methods). Gravimetric methods are taken up in detail in Part III.

Colorimetric analysis consists in making a comparison of the color of the solution containing the desired constituent with the color of a solution containing known amounts of the constituent. These methods are not considered in this book.

By the methods of gas analysis the composition of gas mixtures is determined. Gas analysis involves much specialized apparatus, uses a different technique and usually constitutes a separate course of study.

## THE THEORETICAL BASIS OF QUANTITATIVE ANALYSIS

The first requirement of any quantitative method is that the reaction, which is the basis of the method, run practically to completion. It is true that theoretically all reactions are reversible, as demanded by the Law of Chemical Equilibrium, but only those reactions which are essentially complete can be used for accurate, quantitative methods of analysis. There are several mechanisms by which a reaction runs practically



to completion; expressed in another way, there are several types of reactions in which the equilibrium is reached when the reaction is nearly complete. These types are as follows, and upon these types practically all quantitative methods of analysis are based:

1. Reactions in which a precipitate forms. Gravimetric and volumetric precipitation methods are based on reactions of this kind.
2. Reactions in which a slightly ionized product is formed. Neutralization methods are of this type.
3. Reactions in which a gas or vapor is evolved. Evolution methods are based on this behavior.
4. Reactions between oxidizing and reducing agents. Volumetric oxidation and reduction methods are of this kind.
5. Reactions in which complex ions are produced. There are examples among the volumetric methods, closely allied to precipitation methods.

**The Utilization of Reactions of Qualitative Analysis.** It is to be emphasized at the outset that, whereas these types of reactions are the same as those employed in qualitative analysis for separations and tests, they are used in quantitative analysis for accurate methods of determination, under a more careful regulation of conditions and with greater attention to details. The same general principles which are encountered in the study of the reactions of qualitative analysis are likewise involved in quantitative analysis. In general the specific properties utilized for the qualitative separation and identification of elements become, under exact manipulation, the basis for their quantitative determination. Thus, in many cases, a reaction which serves as an identifying test for a particular ion will be found to be the reaction best suited for the quantitative estimation of that ion. It is therefore important that the student have at his command a thorough understanding of the fundamental principles of qualitative analysis and a good knowledge of the behavior and properties of the elements whose determination is undertaken.

**Ionic Nature of Reactions.** Most of the reactions upon which quantitative methods are based take place in aqueous solutions and are, for the most part, ionic in nature. The solutions of reagents and samples consist, most generally, of solids, liquids or gases dissolved in water. The most important property shown by aqueous solutions of inorganic materials is that the dissolved matter ionizes (dissociates) more or less into electrically charged atoms or groups of atoms called ions, those with positive charges being the cations and those with negative charges being the anions. The extent or degree of ionization varies much with the



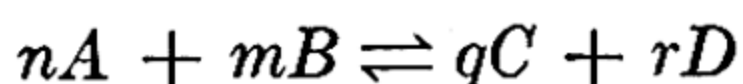
nature of solute and solvent as well as with the concentration and temperature.

The variation in the degree of ionization for acids and bases is very wide, ranging, for example, in tenth-normal solutions from about 90 per cent for strong acids such as HCl and HNO<sub>3</sub> to 1 per cent or less for HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, HCN and H<sub>2</sub>S, and for bases from about 90 per cent for NaOH and KOH to about 1 per cent for NH<sub>4</sub>OH (see table of ionization on page 65). As the dilution increases and the total amount of dissolved compound becomes less for unit volume, the degree of ionization increases. Rise in temperature causes a decrease in ionization for most electrolytes, water being an exception. Salts as a general rule are highly ionized in moderately concentrated solutions.

### THE LAW OF CHEMICAL EQUILIBRIUM

Two fundamental laws of chemistry are involved in practically every quantitative reaction. They are: the Law of Chemical Equilibrium and the Law of Definite Composition. The first of these laws in its several applications enables us to determine whether a reaction runs far enough to completion to make it suitable for a quantitative method of analysis. By means of the second law we are enabled to calculate the amount of constituent sought from the data obtained during the determination.

The Law of Chemical Equilibrium, which is derived from the Law of Mass Action, fixes the equilibrium point of a reaction. For every reaction an equilibrium is reached when the velocity of the reaction forward is just equal to the reaction velocity in the reverse direction and at this point the masses of reacting components bear a definite relation to each other. Thus in the reaction



when equilibrium is reached, the reaction velocity,  $v_1$ , of the forward reaction is equal to the molar concentration of  $A$  raised to the  $n$ th power times the molar concentration of  $B$  raised to the  $m$ th power times a velocity constant,  $k_1$ . Expressed algebraically this relation is

$$v_1 = (C_A)^n \times (C_B)^m \times k_1 \quad (1)$$

Likewise, the velocity with which  $C$  and  $D$  are reacting to produce  $A$  and  $B$  may be expressed thus:

$$v_2 = (C_C)^q \times (C_D)^r \times k_2 \quad (2)$$

Since at equilibrium the velocities are equal, equations 1 and 2 can be equated and we have

$$(C_A)^n \times (C_B)^m \times k_1 = (C_C)^q \times (C_D)^r \times k_2$$

Dividing by the first member and transferring  $k_2$  and  $k_1$  gives the equilibrium ratio

$$\frac{(C_C)^q \times (C_D)^r}{(C_A)^n \times (C_B)^m} = \frac{k_1}{k_2} = K \text{ (equilibrium constant)}$$

This is the most general algebraic expression of the equilibrium law which may be stated thus: When equilibrium is reached in a reacting system, the product of the molar concentrations of the resultants of the reaction divided by the product of the molar concentrations of the reactants, each concentration raised to a power equal to the coefficient representing the number of like reacting parts which enter into the reaction, is always equal to a constant. For each reaction where the law strictly holds, and at a constant temperature and pressure, the numerical value of the equilibrium constant is always the same. No matter how much the concentration of any one component in the reaction mixture may vary, the proportions of the other components must change until equilibrium is again established and the value of the equilibrium constant is restored. Thus, if in the above reversible reaction the amount of  $A$  or  $B$  is increased, the reaction will proceed in the direction of the formation of  $C$  and  $D$ , more of these products will be formed, the reaction will reverse at a faster rate than originally until equilibrium is again established, with the masses of  $A$ ,  $B$ ,  $C$  and  $D$  changed but the ratio of the products of the molar concentrations still the same.

The important applications of the Law of Chemical Equilibrium to quantitative analysis are concerned with the equilibrium conditions which are reached in aqueous solutions. Since most of such reactions are ionic in nature, several types of ionic equilibria are encountered.

**The Equilibrium Law Applied to Ionization.** For weakly ionized electrolytes, such as  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NH}_4\text{OH}$ , the equilibrium law can be rigorously applied, and for each such weak electrolyte the ratio of the product of the gram-ion concentrations of the respective ions to the molar concentration of the non-ionized, dissolved electrolyte is a constant called the **ionization constant**. Expressed algebraically:

$$\frac{C \text{ (cations)} \times C \text{ (anions)}}{C \text{ (non-ionized, dissolved molecules)}} = K_{\text{ion}}$$

For example, for acetic acid we have the ionic equilibrium

$$\frac{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = K_{\text{ion}}$$



This means that in any solution in which there are  $H^+$  ions and  $C_2H_3O_2^-$  ions, the concentrations will adjust themselves, by the formation of  $HC_2H_3O_2$ , such that the ionization constant of acetic acid is satisfied. An important consequence of this relationship is that we are able to regulate the concentration of the  $H^+$  ion, that is, the acidity of the solution, and keep it within fixed definite limits by the addition of a salt such as  $NH_4C_2H_3O_2$  which furnishes a high concentration of acetate ions. This is known as the **common-ion effect**, and solutions used in this way are called **buffer solutions** and are frequently employed in quantitative work.

**The Equilibrium Law Applied to Precipitate Formation.** This very important application of the equilibrium law is involved every time a precipitate forms or dissolves. It is known as the **solubility product principle**. The principle states that in a saturated solution of a slightly soluble salt the product of the gram-ion concentrations of the ions which enter into the composition of the salt is a constant. Expressed algebraically, the relation is

$$C_{\text{cations}} \times C_{\text{anions}} = K_{s.p.}$$

This relationship can be directly derived from the Law of Chemical Equilibrium as a special case of the equilibrium which exists in solutions in which precipitates are forming or dissolving. The principle is of great importance in all gravimetric and volumetric precipitation procedures. A detailed discussion of the solubility product principle and its application to quantitative precipitation are given on pages 161 and 181.

**Other Applications of the Equilibrium Law.** There are still other types of equilibria in reactions in aqueous solutions, to which the equilibrium law applies. In particular the reactions of hydrolysis, in which the ions of water,  $H^+$  and  $OH^-$ , enter into reaction with other ions; reactions in which complex ions are formed; reactions in which amphoteric forms of certain substances play a role; and the reactions between oxidizing and reducing ions are all special cases dealing with particular applications of the equilibrium law. These cases are dealt with in more detail where they are of particular significance in analysis.

## THE LAW OF DEFINITE COMPOSITION

The chemical composition of a pure compound is always the same. That is, a given chemical compound always contains the same elements united together in the same proportions by weight. Thus, if we analyze a unit weight of water, such as 1 gram, we will find it to contain 0.1119

gram, or 11.19 per cent by weight, of hydrogen, and 0.8881 gram, or 88.81 per cent by weight, of oxygen. If we take 18.016 grams of water for analysis, or decompose this quantity by electrolysis or otherwise, we will obtain 11.19 per cent of 18.016 grams or 2.016 grams of hydrogen and 88.81 per cent of 18.016 grams or 16.00 grams of oxygen. From the analysis of all pure compounds, we find it true that the proportion by weight of the elements in a compound is always constant. This fundamental fact of the constancy of chemical composition is embodied in the Law of Definite Composition or Constant Proportions, which may be stated in its simplest form thus: **In any chemical compound the proportion by weight of the constituent elements is always the same.**

This fact is in itself of tremendous importance in analytical chemistry, for if we have a given weight of a pure compound, we know that it is composed of definite proportions of the constituent elements. In order to calculate the proportions present, since in general it is impossible or impracticable to isolate and weigh the constituent elements directly, we must use the atomic weights of the elements involved.

**Atomic weights** are the relative weights of the atoms of the elements and represent the proportions by which they combine with each other. Chemists have fixed the scale of these relative combining weights or proportions on the basis of oxygen as 16. To each element is assigned a number, its atomic weight, which represents the parts by weight (on the arbitrary basis of oxygen = 16) with which that element will combine with other elements. If a particular element unites with another element in more ways than one, the combining proportion is a simple multiple of the atomic weight.

By adopting the system of atomic weights we are enabled to calculate the composition of pure compounds and the proportions by which elements and compounds enter into reaction. Thus, in the case of water, we have seen that the ratio of oxygen to hydrogen is, invariably, 16: (2  $\times$  1.008); that is, 16 parts by weight of oxygen and 2.016 parts by weight of hydrogen. On the basis of the atomic theory, one atom of oxygen unites with two atoms of hydrogen to form water. Atomic weights are directly proportional to the actual weights. This is, in brief, the Law of Combining Weights, which can be stated thus: **Reactions take place between weights of chemical substances which are proportional to the atomic or molecular weights of the reacting elements or compounds.** Thus, if we know the actual weight (in grams, pounds, grains or any other units) of one of the components, we can by a simple direct proportion between the actual weights and the atomic weights calculate the actual weight of the other components of the reaction.



**GENERAL OPERATIONS IN PREPARING SAMPLES FOR ANALYSIS**

**Sampling.** The securing of a representative sample is an important consideration too frequently ignored by the analyst. No general rules can be laid down in regard to sampling, for much depends upon the nature of the material and the quantity from which a representative sample is to be taken. Liquids are best sampled by taking small samples at various levels from the tank or other container. Samples of alloys and metals may best be secured by drilling or chipping from several sections of the sample bar or ladle. Dry powders should be sampled by taking a small scoopful from each sack.

Coarse material such as ores, rocks, coal, etc., may be sampled from the car, bin or dump, about a ton for each carload. This coarse material must then be crushed, placed in a cone-shaped heap, divided into four quarters and two opposite quarters retained. Further crushing and quartering are necessary, the operations being repeated until about five pounds of material of about 60-mesh remain. From this reduced sample the laboratory sample is secured, and sometimes ground to 100-mesh. In grinding it is important to grind all the sample and not discard the more resistant parts. The grinding is best done by a ball mill.

Students' samples, as a rule, are supplied all ready for analysis. Certain samples which require drying should be spread on a large watch glass, thoroughly mixed, and dried in an oven at about 105°C. They should then be placed in a weighing bottle and kept in a desiccator.

The moisture content of certain industrial samples must be determined in order that the results, obtained from the dried sample, can be recalculated for the sample "as received." The procedure for a moisture determination is given on page 48. Further reference is made to moisture determinations on page 217.

**Weighing the Sample.** The most important instrument for the analyst is the balance, since all weighing operations are conducted by means of it. The proper weight of sample to be taken for an analysis must be decided upon for each type of material. The rule which governs this is: Enough sample should be taken to give sufficient constituent so that the operations of volumetric or gravimetric analysis can conveniently be carried out with a single set of apparatus, but not so much that the operations consume too much time. The amount of sample to take is determined by the content of the constituent sought. If the constituent is present in small amount a relatively larger sample must be taken; on the other hand, if the sample contains large amounts, a smaller portion of sample should be taken. The approximate content in the sample can be determined by a well-conducted qualitative analysis. In



students' samples the procedures provide for the proper weight to be taken.

**Dissolving the Sample.** Water-soluble samples ordinarily will present no difficulty in dissolving. In some cases the water must be acidified. Dilute nitric acid is the usual solvent for water-insoluble samples, but in some cases dilute hydrochloric acid is preferable.

Materials which resist acid treatment must be fused to get them into solution. The commonest flux for materials of an acid nature, such as silicates, is  $\text{Na}_2\text{CO}_3$ . For basic materials an acid flux such as  $\text{KHSO}_4$  is used.

## ERRORS AND PRECISION OF QUANTITATIVE METHODS

**Errors.** The accuracy of a quantitative method depends upon how completely the errors introduced in the determination can be reduced. No method is absolutely free from errors no matter how carefully one carries out the procedure. The analyst must know the sources of error in the method used and how certain of these errors may be minimized, in order to determine the relative care with which he must work as well as the reliance he can place on his results.

The errors of an analytical method are of several different kinds, some of which can be reduced to a negligible amount and others which cannot. Errors arising from careless technique such as faulty sampling, mistakes in weighing, incomplete precipitation, washing and ignition, losses of material or inclusion of dust and foreign matter during manipulations, failure to match end points during titrations, disregard of temperatures and mistakes in recording and computing data—all these can be practically eliminated by paying the closest attention to the details of manipulation, by the use of clean apparatus and by developing a certain amount of skill and dexterity in technique.

Errors arising from the use of faulty measuring apparatus such as inaccurate balances, weights and burets can be greatly minimized by making sure that the balance is properly adjusted, and by the calibration of the set of weights and the calibration of burets, flasks and pipets. Certain personal errors, which tend to introduce a constant error in the observations, can also in most cases be corrected.

Errors inherent in the reaction itself can be only partially eliminated. A reaction never runs absolutely to completion; if equilibrium is reached while quantities measurable by ordinary analytical methods still remain, an appreciable error is present in the method. To a certain extent this effect can be counterbalanced by using an excess of precipitating agent, by judicious choice of the indicator in titrations or by some other means, but a certain constant error still remains.

Errors, over which the experimenter has no control, are present in every series of measurements and represent the variations in observations and readings even where every precaution is taken to minimize all other errors. The magnitude of these errors follows the laws of chance and can be shown by a probability curve. It is important that the analyst know how closely a number of similar measurements may be expected to agree with each other and especially how reliable the average result may be. This will give him a measure of the precision of the method.

**Precision and Accuracy.** By precision is meant the agreement in value of two or more similar measurements or observations; precision is most simply indicated by the deviations between two or more individual values. Such deviations can readily be computed by the student during the course of a determination and will show him how consistently he has duplicated the various operations by which the data were derived. The precision does not, however, tell how accurately he has worked.

By accuracy is meant the agreement of individual results (or their average) with the true value. The accuracy of the student's result can only be ascertained by comparing this result with the true content of the sample. The student may obtain a high precision, but by the introduction of a large error, carried through two or more duplicate steps, the accuracy of the final result may be poor.

In quantitative analysis we are just as much concerned with the ultimate effect of all errors on the final result as we are with the deviations of the various measurements which are made during the course of an analysis. In other words, we want to know within what limits check results may be expected to lie. For this purpose the precision is best expressed in parts per thousand. For example, if two determinations give 24.95 and 24.90 per cent, respectively, for the amount of a certain constituent contained in a given sample, and the correct result is 25.00 per cent, the deviations are 0.05 and 0.10, respectively, and the accuracy is 2 parts and 4 parts per thousand.

It is preferable to express the precision in parts per thousand rather than as a percentage of error because the amount of constituent is usually reported as a percentage and confusion is thus avoided.

The accuracy depends, among other things, upon the amount of constituent present; the smaller the amount the poorer the accuracy. For every analytical method the accuracy is known or can usually be determined. In student analyses, precision is apparent from duplicate runs, whereas accuracy is ascertained by the deviation of results from the true value of the sample. The best agreement we can hope for in any ordinary volumetric or gravimetric method is about 1 part in a thousand.



## MATHEMATICAL OPERATIONS

The calculations of quantitative analysis are of several kinds and are dependent upon the nature of the method used. The most important type of calculation is that based on the Law of Definite Composition, and such a calculation must be made with the data of every quantitative determination; fundamentally the calculation involves a direct proportion between actual weights and molecular or atomic weights. Second in importance are the calculations involving applications of the Law of Chemical Equilibrium and dealing with precipitation, regulation of ion concentrations, buffer solutions, etc. Certain electrochemical methods require computations based on the laws of electrochemistry and certain gas analytical methods involve the gas laws. Examples of these various types are given later in problem sets and applied to the data of the procedures.

In the present section attention is directed to computation rules with special reference to significant figures and to the use of exponents and logarithms.

**Significant Figures.** Significant figures are the digits which when placed in order give the value to a number. Thus in the quantity represented by the number 635, the digits 6, 3 and 5 are significant figures. Zeros are used in some cases to locate the decimal point; in others they may be significant figures. In the number 30.25, the zero is a significant figure; in 0.015 the zeros are not significant but show the order of magnitude represented by the other digits. Zeros following other digits may or may not be significant.

The ordinary analytical balance weighs to one-tenth of a milligram, that is, to the fourth decimal place; hence only four digits to the right of the decimal point, in the weight of an object, are significant. A buret can be estimated to one one-hundredth of a milliliter; hence two digits to the right of the decimal point are significant. In general, percentages are usually calculated to the nearest 0.01 per cent.

**Computation Rules.** In making computations from the data of an analysis, it is important that the proper number of significant figures shall be retained and the superfluous ones discarded, in order that the result may properly represent the degree of precision of the determination.

In general each quantity should contain only such a number of significant figures as to have the last one uncertain. Thus, in a buret reading of 30.25 ml. the last digit, 5, is estimated and hence uncertain, but should be retained. When superfluous digits are discarded, increase by 1 the last figure retained if the discarded figure is 5 or more.

In adding or subtracting numbers, retain in each number only those corresponding to the uncertain figure in the number having the least number of digits to the right of the decimal point. For example, when adding together 30.25, 1.062 and 6.7685, the quantity which determines the number of significant figures to retain is 30.25; modifying the above quantities to read  $30.25 + 1.06 + 6.77$ , the sum becomes 38.08.

In multiplying or dividing retain as many significant figures as are contained in the quantity having the least number of significant figures.

**Use of Exponents.** In certain types of chemical calculations, involving extremely large or extremely small numbers, it is very cumbersome to carry out the arithmetical operations in the ordinary way. Solubility data, ionization and other equilibrium constants and certain other data of physics and chemistry are frequently obtained with a precision good only to one, two, three or at most four significant figures, yet the actual magnitudes may be extremely small or large. Such quantities are best expressed in the exponential form, the arithmetical work which follows being then much simplified.

It is assumed that the student is already familiar with exponents. The rules in their use are briefly summarized below.

When multiplying two or more quantities, express each in the exponential form and *add the exponents*. The significant figures must of course be treated in the ordinary way. In multiplications involving negative exponents, the *algebraic sum* is taken.

When dividing one quantity by another *subtract the exponents* algebraically.

When an operation involving both multiplication and division is necessary, express each quantity in the exponential form, transfer the exponents from the denominator to the numerator with change of sign and take the algebraic sum of the exponents.

In raising numbers to a specified power, the exponents are doubled for squaring, trebled for cubing, etc. In extracting roots, the exponent is divided by 2 to obtain the square root, by 3 for the cube root, etc.

**Use of Logarithms.** The solving of problems and of the results of determinations from analytical data is greatly facilitated by the use of logarithms, and it is strongly advised that students use this method. To those not familiar with logarithms, it may be said that many hours of tedious long-hand computation may be saved by acquiring a working knowledge of this very helpful mathematical device.

A logarithm is an exponent which must be applied to a number, known as the base, in order to produce any given number. In the common or Briggsian system of logarithms, the base is 10. Thus in the equation

$$10^2 = 100$$



the exponent 2 is the logarithm of 100, when the base is 10. The above equation, in terms of logarithms, can then be written:

$$\log_{10} 100 = 2$$

which states that the logarithm of 100 to the base 10 is 2. The relation of exponential to logarithmic forms for simple, whole numbers as exponents is shown in Table I.

TABLE I

<i>Number</i>	<i>Exponential Form</i>	<i>Logarithm</i>
1,000,000	$10^6$	6
1,000	$10^3$	3
100	$10^2$	2
10	$10^1$	1
1	$10^0$	0
0.1	$10^{-1}$	-1
0.01	$10^{-2}$	-2
0.001	$10^{-3}$	-3
0.000001	$10^{-6}$	-6

Note that the logarithm of 10 is 1, that of 1 is 0 and that for negative exponents there result corresponding negative logarithms.

A logarithm is made up of two parts: the *mantissa*, which is found in logarithm tables and which is placed to the right of the decimal point; and the *characteristic*, which is placed to the left of the decimal point. In four-place log tables, the mantissas are given to four decimal places. The log table in this book is a five-place table and is to be used in making the calculations based on the laboratory data. Illustrative calculations as well as answers to problems in this book are based on four-place logs.

In making computations by logarithms, the logs of the numbers must first be found. Then, if an operation of multiplication is to be made, the logs are added; if a division is called for, the logs are subtracted; and to raise a number to a certain power, the log is multiplied by that power. Finally, the number corresponding to the final logarithm is ascertained, as illustrated below, from log tables; a table of antilogarithms is sometimes used for this purpose.

To write the logarithm of a number, first supply the characteristic. For numbers greater than unity, the characteristic is one less than the number of digits in the given number. Thus,

$$\log \text{ of } 10 = 2 - 1 = 1.0 \dots$$

$$\log \text{ of } 100 = 3 - 1 = 2.0 \dots$$

$$\log \text{ of } 1000 = 4 - 1 = 3.0 \dots$$

For numbers such as 5, 55, 555, 5555 and 55555, the characteristics are, respectively, 0, 1, 2, 3 and 4; the mantissas must be supplied from log tables. For the first four examples cited, the mantissas are given directly in the five-place log tables in the Appendix and are tabulated below. Interpolation is necessary for numbers such as 55555. Here we must interpolate between the logs of 5555 and 5556. The difference is 0.00005. The difference between the mantissas 74476 and 74468 is .00008. In the "Proportional Parts" column of the log table, under "8" it is found that a difference of 0.00005 or (5) in the original number corresponds to "4.0" or 0.00004. This is then added to the mantissa 74468, giving a mantissa of 74472 for the number 55555.

The logarithms of these illustrative numbers are then

$$\log 5 = 0.69897$$

$$\log 55 = 1.74036$$

$$\log 555 = 2.74429$$

$$\log 5555 = 3.74468$$

$$\log 55555 = 4.74472$$

Numbers less than unity have negative characteristics. The characteristic for decimal numbers, having no zeros immediately following the decimal point, is designated as  $\bar{1}$  or 9 (plus mantissa)  $- 10$ . For example, the logarithm of 0.50000 would be written  $\bar{1}.69897$ , or  $9.69897 - 10$ .

If in a given number there are no digits before the decimal point and  $n$  zeros before the significant figures after the decimal point, the characteristic is  $(1 + n)$  or  $(9 - n)$  plus mantissa  $- 10$ . For example, the log of 0.05500 is  $\bar{2}.74036$  or  $8.74036 - 10$  and the log of 0.000555 is  $\bar{4}.74429$  or  $6.74429 - 10$ . The use of the system involving  $(9 - n) - 10$  is recommended to students.

The logarithms of some decimal fractions are here tabulated.

$$\log \text{ of } 0.50000 = \bar{1}.69897 \text{ or } 9.69897 - 10$$

$$\log \text{ of } 0.05500 = \bar{2}.74036 \text{ or } 8.74036 - 10$$

$$\log \text{ of } 0.00555 = \bar{3}.74429 \text{ or } 7.74429 - 10$$

$$\log \text{ of } 0.000555 = \bar{4}.74468 \text{ or } 6.74468 - 10$$

$$\log \text{ of } 0.055555 = \bar{2}.74472 \text{ or } 8.74472 - 10$$



It should be noted that the logarithm of a decimal fraction such as 0.05500, as expressed above, consists of a negative characteristic, written  $\bar{2}$ , or  $8 - 10$ , and a positive mantissa (.74036). This might also be written as a negative logarithm by adding the two parts, algebraically, giving  $-1.12563$ .

The finding of the number (antilogarithm) corresponding to a given logarithm is, in general, the reverse of finding a logarithm. For logs having positive characteristics, look up in the log table the number corresponding to the given mantissa and adjust the decimal point. For example, in finding the antilogarithm of  $\log 3.74468$ , we find that 74468 (in the log table) is the mantissa of 5555. Since the given log has a characteristic of 3, the desired number has 4 digits to the left of the decimal point and the number is 5555. Likewise, the antilog of 1.74468 is 55.55.

For logarithms having negative characteristics, such as  $7.74429 - 10$  or  $\bar{3}.74429$ , look up the number in the log table corresponding to the mantissa; this will be found to be 555. Since the characteristic is  $\bar{3}$ , the number sought is 0.00555.

The rule for locating the decimal point, for numbers having positive characteristics, is to place  $n + 1$  digits before the decimal point, where  $n$  is the characteristic. For negative characteristics, place  $n - 1$  zeros after the decimal point.

A logarithmic calculation, typical of many similar ones encountered in the laboratory and problem work, is illustrated here.

Find the result of the following indicated operations:

$$\frac{25.62 \times 0.1234 \times 0.05300}{0.2013} \times 100$$

$\log 25.62$	$=$	1.40858
$\log 0.1234$	$=$	9.09132 - 10
$\log 0.05300$	$=$	8.72428 - 10
$\log 100$	$=$	2.00000
Adding:		<u>21.22418 - 20</u>
$\log 0.2013$	$=$	<u>9.30384 - 10</u>
Subtracting:		12.92034 - 10
or		1.92034
antilog	$=$	83.242
or		83.24



### THE ANALYTICAL BALANCE

The analytical balance, by which all weighings are made, is the most important piece of apparatus in the quantitative laboratory. Since the accuracy of an analysis depends so largely on correct weighings, a proper understanding of the construction, use and care of the balance is essential. Balances differ a great deal in details of construction and in sensitiveness, depending upon the use to which they are to be put. The analytical balance in common use weighs to the fourth decimal place, that is, to 0.0001 of a gram. The assayer's balance weighs to the fifth decimal and a microchemical balance to the sixth decimal place.

**The Mechanical Features of the Ordinary Balance.** The balance operates on the principle of the lever. A beam of light truss work, to the center of which is attached an agate knife-edge, rests upon an agate plate. The beam carries at each end a stirrup with a knife-edge, the two stirrups supporting the pans upon which the weights and object are placed. The combination as a whole acts as a lever and fulcrum.

The essential parts of the balance and their function are shown in the accompanying sketch.

A good balance in order to give accurate and satisfactory service must have the central knife edge and the terminal knife edges in the same horizontal plane. The knife edges must remain true and not become blunted or injured by rough treatment. The arms must be of equal length. The center of gravity must lie slightly below the central knife edge. The balance must oscillate fairly rapidly. The sensitiveness should be such that an extra load of one milligram on one pan displaces the pointer about three pointer-scale divisions.

Before attempting any weighings examine the balance assigned to you and study its construction and then check up the following points.

1. See that the balance is level as indicated by the plumb bob or spirit level. If it is not, adjust it by means of the screw supports on the base.

2. Test the beam support and the pan arrests for smooth operation.

3. Check over the weights in the weight box and familiarize yourself with the units. See that the rider is of proper weight for the balance.

4. With balance door closed, release the beam and pans and start the pointer to swinging. If the balance is properly adjusted the pointer should swing equal distances on either side of the zero mark on the pointer scale. The point of ultimate rest must be determined as described below.

**Point of Rest.** When the balance is in equilibrium the pointer will come to rest at some point on the pointer scale. In perfect adjustment

this point of rest will coincide with the zero position of the scale. In practice a displacement of one small scale division between the actual and the marked zero is permissible. The point of rest must be determined each day the balance is used. This is done as follows: Set the

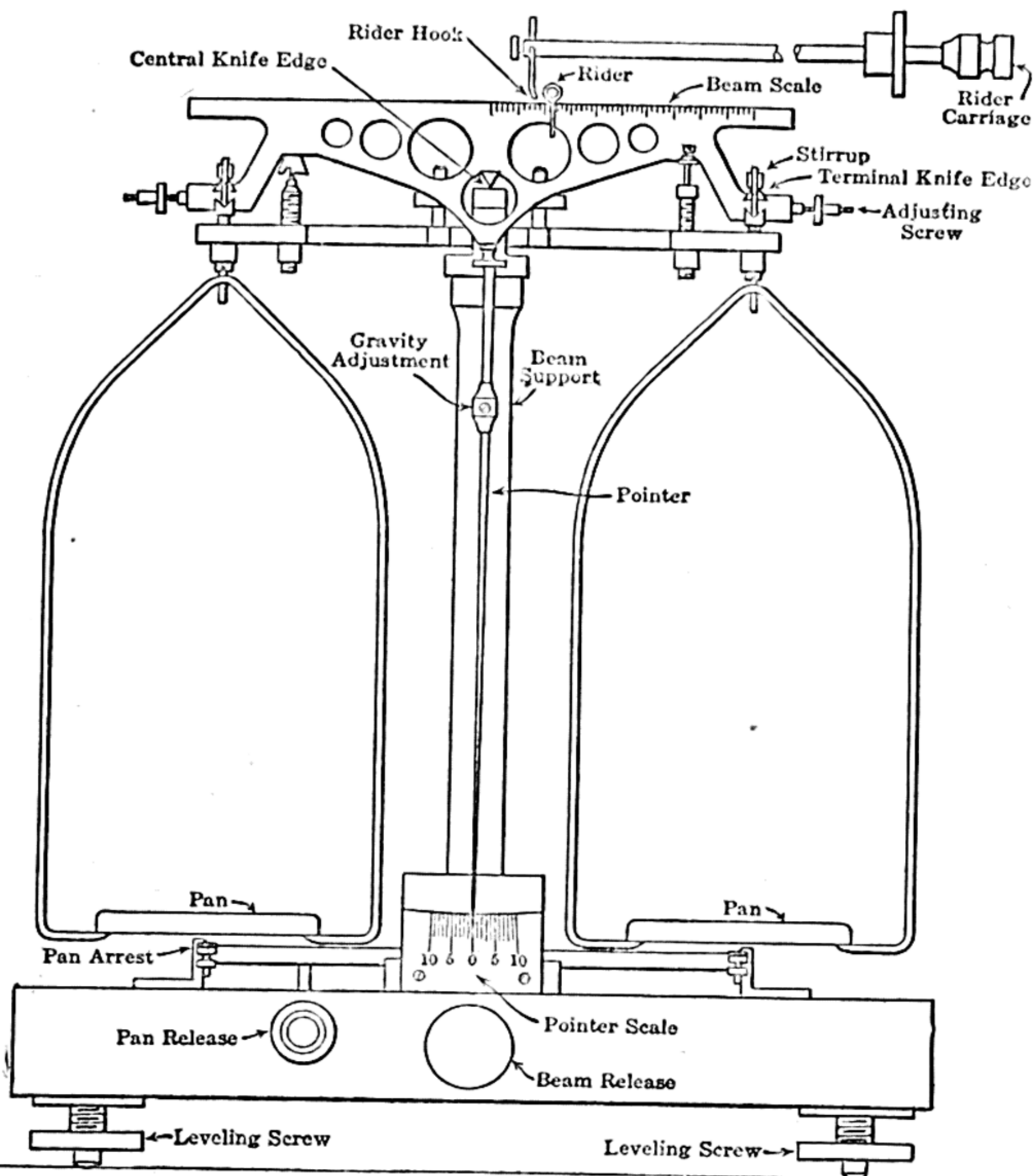


FIG. 1. Essential parts of an analytical balance.

pans in motion, with no load on either pan, so that the pointer traverses at least five scale divisions on either side of the zero. When the pointer is swinging freely take a reading of the pointer position at the end of the oscillation to the left and a reading to the right; take the difference and divide by 2.

For instance, suppose the pointer swings to 5.9 on the left and 5.3 on the right. The difference is 0.6 and therefore the point of rest is 0.3 scale divisions to the left of zero.



For the case here illustrated the balance is in satisfactory adjustment. If it is off by more than one whole scale division, ask the instructor to adjust the balance. This is done by moving the small thumb nut on the extremity of the beam, thereby adding or subtracting weight from one of the pans.

**Sensitivity.** The sensitivity depends largely upon the length of the beam arms and is indicated by the amount of displacement of the pointer when a small excess load is placed on one of the pans. It is usually defined as the number of scale divisions the pointer is displaced from its point of rest when an additional weight of 1 milligram is placed on the pan or the rider is moved one whole division (1 mg.) to the right. Further instructions are given on page 46.

**Rules for Weighing.** 1. See that the inside of the balance case and the pans are clean and free from dust and, if not, use the large camel's hair brush supplied for this purpose. See that the release is working properly.

2. Determine the point of rest; have the instructor make any needed adjustments.

3. Place the object to be weighed on the left-hand pan. Samples of dry material may be weighed on a weighed watch glass, kept for this purpose, or from weighing tubes. Never place material directly on the pan.

4. Always use the forceps for handling objects and weights and never touch them with the fingers.

5. Whole and fractional weights should be added to the right-hand pan, starting with the largest weight. Never change weights or remove the object being weighed without first arresting the pans and placing the beam on its support.

6. Close the door and adjust the rider until the swings of the pointer are equal on both sides of the zero position. Never move the rider while the beam is suspended on the knife-edges.

7. Add up the weights missing from the box and check this against the weights as they are replaced after the object is weighed.

8. Do not weigh hot, wet or recently rubbed objects. Hot air currents, varying humidity and electrical effects will introduce large errors.

9. Make sure the beam and pan arrests are restored before leaving the balance.

10. Keep the balance clean and in the best of condition. The weights require the same care.

11. Remember that the balance is a delicate instrument but will give you satisfactory service if not abused. Regard it as your personal property even though others may be assigned to it.



**Calibration of Weights.** For work demanding reasonable precision, the weights should be calibrated. It is not necessary in ordinary work that all the weights be absolutely correct with the international standard of weight, but they must be accurate among themselves. The units of an ordinary inexpensive set are usually in slight error and corrections should be applied to them. A calibration should be made by comparing them with each other, using as the starting point one of the centigram weights and assuming that this weight is correct. In a one-semester course of instruction, the calibration of weights must be dispensed with.

To calibrate a set of weights, first mark the duplicate weights of like denominations with punch marks so that they may be identified. Then place a centigram weight assumed to be correct on the left-hand pan and balance it against a suitable tare. The most convenient tare to use is the weights from another set. To balance the first centigram weight, which is taken as the temporary standard (assumed correct) weight, place a tare of somewhat less than 0.0100 gram on the right-hand pan and use the rider to establish equilibrium. Then replace the first centigram weight by the second centigram weight of the set, which is marked 0.01<sup>1</sup>, and move the rider until the point of rest is again established. The amount by which the rider was moved is the difference in weight between the two 1-centigram weights. Suppose that in balancing the second 0.01 gram weight against the tare the rider was moved from 3.2 to 3.5, a distance corresponding to 0.3 of a milligram. Assuming the first centigram weight to be correct, the second centigram weight therefore weighs 0.0103 gram, that is, it is 0.0003 gram too heavy.

Next place both centigram weights on the left-hand pan and weights from the auxiliary set on the right-hand pan until the load is almost balanced and then balance with the rider. The mass now on the left-hand pan is  $0.0100 + 0.0103$  gram. Now exchange the two 1-centigram weights for the 2-centigram weight, and move the rider until the loads are balanced. Suppose the rider must be moved one small division (0.1 milligram) to the right; then the weight of the 2-centigram weight in terms of the temporary standard is  $0.0203 + 0.0001$  or 0.0204 gram.

In the same way determine the relative mass of the second 2-centigram weight (marked 0.02<sup>1</sup>). Suppose it is found to be 0.0203 gram.

To standardize the 0.05-gram weight against the temporary standard, place the standard 0.01, the 0.02 weight which weighs 0.0204 gram and the 0.02<sup>1</sup> weight which weighs 0.0203 gram, on the left-hand pan, making a total weight of 0.0507 gram, and balance with a tare and the rider. Replace these weights by the 5-centigram weight and balance with the rider. If the rider must be moved, say two small divisions to the left, the value of the 5-centigram weight is 0.0505 gram.



Proceed in this way with the comparison of each weight, building up combinations as the larger weights are determined. Tabulate the value of each weight as compared with the first centigram weight as the assumed standard. Since the unit chosen as the standard is small, it is better to calculate the correction which must be applied to each weight, in terms of a weight of a larger denomination, for which a 10-gram weight is usually used. If it is desired, moreover, to have the set of weights agree, not only among themselves but with the standard of the Bureau of Standards, include in the comparison a 10-gram weight from a set furnished by the Bureau of Standards. The 10-gram weight which is now selected as the permanent standard, either the weight from the set or a standard 10-gram weight, when compared with the combination of smaller weights, by the method of substitution used above, will have an apparent mass greater or less than exactly 10 grams. Suppose the summation of the smaller weights gives to the selected standard a mass of 10.0150 grams.

To find the true value of each weight in the set, compute the aliquot part of 10.0150 corresponding to each weight. Thus, in the present case, the aliquot part for each 10-gram weight is 10.0150; for the 5-gram weight is 5.0075; for the 1-gram weights, 1.0015; for the 0.1-gram weights 0.10015; and so for all other weights in the set.

The correction which must be applied to each weight whenever it is used in subsequent weighings is then found as the difference between the apparent weights as previously determined and the proper aliquot part of the standard. To illustrate this, in the data above the 0.05-gram weight was found to have an apparent value of 0.0505 gram and the aliquot part of the standard is 0.050075; the difference is 0.000425. The correction to apply is therefore  $+0.0004$  gram, and this value must be added to the face value (0.0500) of the 0.05-gram weight. If the difference in any case is a negative value, it must be subtracted from the face value of the weight.

A table of corrections should be placed on a card and kept in the balance case.

**Correction for Buoyancy.** For very precise work, weighings must be corrected for the buoyancy of the air, that is, weights must be reduced to vacuo. The apparent weight of an object in air is less than its true weight by an amount equal to the weight of the volume of air displaced. A milliliter of air, under ordinary laboratory conditions, weighs 0.0012 gram. The volume of air displaced by an object is equal to its weight divided by its density. Since the object being weighed is counter-balanced by brass weights, which also displace a certain volume (and weight) of air, the true weight of the object, that is, the weight it would



have in a vacuum, is equal to its weight in air plus the difference in the weights of air displaced by the object and by the weights.

If, for example, a porcelain crucible weighs 7.6252 grams in air, what is its weight in vacuo? The density of porcelain is 2.4 and that of brass weights approximately 8.0. The volume of air displaced by the crucible is  $7.6252/2.4 = 3.17$  ml., and the weight of air is  $3.17 \times 0.0012 = 0.0038$  gram. The volume of air displaced by the weights is  $7.6252/8.0 = 0.95$  ml., and its weight is  $0.95 \times 0.0012 = 0.0011$  gram. The difference, 0.0027, is the buoyant effect of the air. The true weight of the crucible is therefore  $7.6252 + 0.0027 = 7.6279$  grams. The above steps can be combined into the single equation

$$\begin{array}{c} \text{Weight} \\ \text{in} \\ \text{vacuo} \end{array} = \begin{array}{c} \text{Weight} \\ \text{in} \\ \text{air} \end{array} + \left( \frac{\text{Weight in air}}{\text{Density of object}} - \frac{\text{Weight in air}}{\text{Density of weights}} \right) 0.0012$$

It should be noted that if the volume, and hence the weight, of air displaced by the weight is greater than that displaced by the object, the object will weigh less in a vacuum than in air.

## REAGENTS

An important part of every chemist's work is the preparation of reagents. Reagent solutions are made in some cases from the solid chemicals by dissolving the required amount of the solute in water; in other cases, as with the common acids, the reagent is made by dilution of the concentrated solution. The strength of the reagent is an important consideration in every procedure, and as a general rule the strength is so adjusted to the amount of material with which it is to react that the volume of the resulting solution is not abnormally large. Since in many procedures limitations must be placed on the volume of the solution, the reagent must contain enough active reacting substance so that not more than 75 or 100 ml. may be used. For the procedures given in this book reagents of suitable strength are specified, but in devising new methods of analysis the analyst must decide for himself the proper strength to use.

The strength of the reagent is most simply expressed in terms of the grams of solute actually contained in 1 ml. of the reagent or the number of grams of material with which 1 ml. of the reagent will react. The strength in grams per milliliter is known as the **titer** of the solution.

**Reagents Made from Solid Chemicals.** This type of reagent is easily made by dissolving the required weight of pure, previously tested, salt in water (or acids if demanded) and diluting to the desired volume with



distilled water. Calculations involving the strength of reagents of this type are illustrated in the following problem.

What is the strength of a  $\text{AgNO}_3$  solution containing 20 grams of  $\text{AgNO}_3$  per liter, in terms of the amount of chloride ion with which 1 ml. will react?

Since the solution contains 20 grams of  $\text{AgNO}_3$  per liter, 1 ml. contains 0.020 gram. This quantity will react with  $x$  grams of  $\text{Cl}^-$  ion. We then have the relation

$$\begin{array}{ccc} \text{AgNO}_3 : \text{Cl} = 0.02 : x \\ 169.9 \quad 35.46 \end{array}$$

from which  $x = 0.0048$  gram. Therefore 1 ml. of  $\text{AgNO}_3$  will bring into reaction and precipitate as  $\text{AgCl}$  0.0048 gram of chloride ion. This is the chloride-titer of the  $\text{AgNO}_3$  solution.

**Reagents Made by Dilution.** Dilute solutions of hydrochloric, nitric, sulfuric and certain other acids and of ammonium hydroxide, so often employed in analytical procedures, are prepared by diluting the concentrated reagent. The proper amount of water to add to the concentrated stock reagent in order to give a dilute solution of the desired strength must be calculated for each individual case.

Concentrated hydrochloric acid is manufactured by dissolving hydrogen chloride (hydrochloric acid gas) in water until the solution is saturated. The saturated solution contains 39.11 per cent by weight of  $\text{HCl}$  and has a specific gravity of 1.20. The ordinary "concentrated" acid as supplied to the laboratory is somewhat weaker, and for purposes of calculation may be assumed to have a specific gravity of 1.19 corresponding to 37.23 per cent by weight of pure  $\text{HCl}$ .

Concentrated sulfuric acid is the result of the reaction between sulfur trioxide and water. The liquid may be theoretically 100 per cent pure  $\text{H}_2\text{SO}_4$ , and may even dissolve additional amounts of  $\text{SO}_3$ , forming fuming sulfuric acid. The "concentrated" reagent as supplied is somewhat impure, owing to the fact that it readily absorbs water. It may be assumed to be 95.60 per cent pure  $\text{H}_2\text{SO}_4$  and to have a specific gravity of 1.84.

The concentrated nitric acid supplied to the laboratory usually has a specific gravity of 1.42 and contains 69.77 per cent by weight of pure  $\text{HNO}_3$ .

Ammonium hydroxide, as supplied commercially, contains about 28.33 per cent  $\text{NH}_3$  by weight and has a specific gravity of 0.900. The strength of ammonium hydroxide and of acid reagents is usually indicated by the specific gravity of the solution. The specific gravity is the ratio of the weight of a given volume of the liquid to the weight of an

equal volume of water. If the weight of a unit volume of water, 1 ml., is taken as 1 gram, the specific gravity, or rather the density of a liquid, is expressed directly as the weight in grams per milliliter of the liquid. The relation between specific gravity and the percentage by weight of the active constituent and the way these quantities vary with dilution must be ascertained from specific gravity tables such as those found in the Appendix.

If the strength is given in terms of specific gravity, refer to tables to find the percentage of solute or of active constituent. To find the weight of constituent in 1 ml., multiply the specific gravity by the percentage by weight. To illustrate, the grams of HCl in 1 ml. of hydrochloric acid of specific gravity 1.100 is found by reference to the acid table in the Appendix. This is found to be 20.01 per cent. We have then

$$1.100 \times 0.2001 = 0.2201 \text{ gram per ml.}$$

Problems involving data in which the strength of the solution is given in terms of specific gravity are then readily solved by finding the weight present or required per milliliter of the reacting solution.

**Problems of Dilution.** When a concentrated solution is mixed with water the resulting volume will not be equal to the sum of the original volume of the solution plus the volume of the added water. A contraction or expansion takes place upon mixing, making the final volume of the diluted reagent either less or greater than the sum of the volumes of the two original liquids. For example, if 100 ml. of concentrated hydrochloric acid are mixed with 100 ml. of water or dilute acid, the final volume is not 200 ml. as might be expected, but is somewhat less, depending upon the strength of the concentrated acid. The fact that a change in volume results must be kept in mind in making calculations dealing with dilution. A calculation based on the assumption that no volume change occurs is wrong. Weights, however, do not change, and calculations must be made on a weight basis.

The correct way of solving dilution problems is shown by the following example.

How much water must be added to 50 ml. of concentrated hydrochloric acid having a specific gravity of 1.190 and containing 37.23 per cent of HCl by weight in order to make a solution of specific gravity 1.12 containing 23.82 per cent by weight of HCl?

To solve this we must make an equation between *weights*; since no loss or gain of weight takes place during the mixing of the two liquids, and since the total weight of pure HCl does not change on dilution, it is best to equate the amount of pure HCl in the original acid and in the diluted solution.



One milliliter of the original acid weighs 1.19 grams and 50 ml. weigh  $50 \times 1.19 = 59.50$  grams. The weight of pure HCl is therefore  $59.50 \times 0.3723 = 22.152$  grams.

Let  $x$  be the amount of water to add. Then the final solution will weigh  $(59.50 + x)$  grams. It should contain 23.82 per cent of pure HCl. Combining the above steps, and solving for  $x$ :

$$50 \times 1.19 \times 0.3723 = (50 \times 1.19 + x)0.2382$$

$$22.152 = 14.173 + 0.2382x$$

$$x = 33.5 \text{ grams (or ml.) of water}$$

The calculation is somewhat more complicated when the second liquid is a solution of acid instead of water. Suppose, for example, that 50 ml. of hydrochloric acid of specific gravity 1.19 were mixed with hydrochloric acid of specific gravity 1.10 so that the resulting solution had a specific gravity of 1.14. How much of the second acid was used?

The percentages by weight corresponding to the specific gravities of these three solutions, are, from the acid tables (see Appendix):

$$1.19 \text{ sp. gr.} \approx 37.23 \text{ per cent}$$

$$1.10 \text{ sp. gr.} \approx 20.01 \text{ per cent}$$

$$1.14 \text{ sp. gr.} \approx 27.66 \text{ per cent}$$

Let  $x$  equal the volume of the second acid solution. Then equating the weights of pure HCl we have

$$(50 \times 1.19 \times 0.3723) + (x \times 1.10 \times 0.2001) = [(50 \times 1.19) + (x \times 1.10)]0.2766$$

and solving, we find  $x = 67.7$  ml., the volume used.

### PROBLEM SET 1

1. With due regard to significant figures, indicate the proper recording of the following data:

- |   |                          |
|---|--------------------------|
| (a) 32.523 ml. when referred to a buret reading.          | <i>Ans.</i> 32.52 ml.    |
| (b) 2.5 grams weighed on the analytical balance.          | <i>Ans.</i> 2.5000 grams |
| (c) 50 ml. when measured in a measuring cylinder.         | <i>Ans.</i> 50 ml.       |
| (d) 0.00255 gram when referred to an analytical weighing. | <i>Ans.</i> 0.0026 gram  |

2. Find the sum of the following numbers, and record the result with the correct number of significant figures.

$$23.382 + 0.26 + 1.2346 + 1.0 + 11.28 =$$

3. A student carrying out a determination for the percentage of a constituent uses the usual apparatus and weighs to the fourth decimal place; he reports the result as 42.937 per cent. How should the result be reported? *Ans.* 42.94 per cent



4. The following results were found in a student's notebook: Reported 42.65 per cent and 42.92 per cent on duplicate determinations of a material known to contain 42.81 per cent. What was the accuracy in parts per thousand for each determination? What was the precision?

5. (a) If in measuring 10.00 ml., an error of 0.10 ml. is made, what is the percentage error in the measurement? (b) If the same error is made in measuring 25.00 ml.? (c) If in measuring 40.00 ml.?

*Ans.* (a) 1 per cent  
(b) 0.4 per cent  
(c) 0.25 per cent

6. Rewrite the following quantities in the exponential form, retaining the proper number of significant figures.

- (a) 0.000246
- (b) 40 million
- (c) 400 thousand
- (d) 0.0180
- (e) 3250

7. Convert the following exponential quantities into the ordinary form. Retain the proper number of significant figures.

- (a)  $1.240 \times 10^2$
- (b)  $3.76 \times 10^{-4}$
- (c)  $9.6540 \times 10^4$
- (d)  $573 \times 10^3$
- (e)  $37.6 \times 10^{-4}$

*Ans.* (a) 124.0  
(b) 0.000376  
(c) 96540  
(d) 573 thousand  
(e) 0.00376

8. Find the common logarithms of the following numbers:

- (a) 3654
- (b) 0.004231
- (c) 1.569
- (d) 0.9659
- (e) 22.469

9. Find the antilogarithms corresponding to the following logarithms:

- (a) 4.8692
- (b) 0.9681
- (c) 1.6322
- (d)  $7.8643 - 10$
- (e)  $27.8312 - 30$

*Ans.* (a) 73990  
(b) 9.292  
(c) 42.87  
(d) 0.007316  
(e) 0.006779

10. Use logarithms to perform the following operations which are arranged as typical analytical data. Retain the proper number of significant figures.

$$(a) \frac{32.30 \times 0.1142 \times 0.05300 \times 100}{0.2500} = ?$$

$$(b) \frac{0.2845 \times \frac{107.88}{169.89}}{33.03} = ?$$

$$(c) \frac{0.2253}{35.45 \times 0.1699} = ?$$

11. How much (a) CNS is contained in 100 grams of KCNS; (b) Cr in 35.0 grams of  $K_2Cr_2O_7$ ; (c) Cl in 10 grams of pure hydrogen chloride? *Ans.* (a) 59.8 grams

(b) 12.4 grams

(c) 9.7 grams

12. What weight of hydrogen chloride is contained in 20 ml. of hydrochloric acid which has a specific gravity of 1.175 and contains 34.42 per cent HCl by weight?

13. What weight of  $NH_3$  is contained in 20 ml. of ammonium hydroxide solution which has a specific gravity of 0.942 and contains 15.04 per cent of  $NH_3$  by weight?

*Ans.* 2.83 grams

14. What volume of concentrated  $NH_4OH$  is required to precipitate the iron as  $Fe(OH)_3$  in a sample of pure  $Fe_2O_3$  weighing 0.4500 gram?

15. Concentrated HCl has a specific gravity of 1.190 and contains 37.23 per cent hydrogen chloride by weight. What volume of concentrated HCl is required to furnish 3.646 grams of hydrogen chloride? *Ans.* 8.230 ml.

16. It is desired to prepare a solution of nitric acid of specific gravity 1.18 containing 29.37 per cent  $HNO_3$  by weight. How much water must be added to 100 ml. of nitric acid of specific gravity 1.42 containing 69.77 per cent  $HNO_3$  by weight to give the required strength?

17. If it required 85.0 ml. of dilute HCl to precipitate as AgCl the silver in 0.3000 gram of  $AgNO_3$ , how much concentrated HCl was used in the preparation of the dilute acid? *Ans.* 0.145 ml.

18. How much water must be added to 50 ml. of aqueous ammonia of specific gravity 0.900 containing 28.33 per cent by weight of  $NH_3$  to give a solution of specific gravity 0.960 containing 9.91 per cent  $NH_3$  by weight?

19. If 20 ml. of nitric acid (sp. gr. 1.20) are mixed with 20 ml. of aqueous ammonia (sp. gr. 0.95) what is the weight of the excess basic or acidic constituent present?

*Ans.* 0.33 gram  $NH_3$

20. What volume of concentrated hydrochloric acid should be taken to prepare a liter of solution 35.00 ml. of which will neutralize 0.2500 gram of pure  $Na_2CO_3$ ?

*PART II*  
*VOLUMETRIC ANALYSIS*

CHAPTER II  
THE THEORY, TECHNIQUE AND CALCULATIONS  
OF VOLUMETRIC ANALYSIS

In the volumetric methods of analysis the weight of reagent necessary to complete a chemical reaction is ascertained by determining the volume of solution required to react with the material being analyzed, and from this weight the amount of desired constituent in the sample can be calculated. The method, in short, involves adding measured amounts of the reagent to a suitable weight of the sample until the reaction is complete. The strength of the reagent must be accurately known and its total volume carefully measured. Some visible means must be provided for determining when the reaction is completed. The process of determining the exact volume required is called titration. Volumetric methods are also known as titration methods.

THE THEORY OF VOLUMETRIC ANALYSIS

**Classification of Volumetric Methods.** Reactions which are used as the basis of volumetric methods of analysis must go practically to completion. A number of reactions in which precipitates or complex ions are formed, reactions between acids and bases and a great many reactions between oxidizing and reducing substances are among those which readily adapt themselves to volumetric technique. Most of the volumetric methods are of these three types:

1. Neutralization methods.
2. Oxidation-reduction methods.
3. Volumetric precipitation methods.

Neutralization methods have for their object the determination of the acidity or basicity of materials.



Oxidation-reduction methods involve reactions between oxidizing and reducing substances and constitute the most important class of volumetric methods.

In volumetric precipitation methods the exact volume and hence the exact weight of precipitating agent required to precipitate the desired ion or to cause a precipitate to form a complex ion is made the basis of the method.

**Equilibria in Volumetric Reactions.** The equilibria set up in a reacting system determine whether the reaction is sufficiently complete to serve the purpose of a quantitative determination. If equilibrium is reached when appreciable amounts of the initial reactants still remain, the reaction must of course be discarded as a means of determination and other methods of analysis sought. The first requirement of every volumetric method is that the reaction must be practically irreversible.

In neutralization methods, the fundamental theory to be considered is the equilibrium between  $H^+$  ions and  $OH^-$  ions and their possible reaction with the ions of weakly ionized acids and bases. We are primarily concerned in this respect with the ionization constants of water, acids and bases and to a certain extent with hydrolysis constants. Application of ionic theory to the determination of acids and bases is taken up in Chapter III.

In reactions between oxidizing and reducing agents equilibria are likewise set up which determine to what extent such reactions are complete.

The Law of Chemical Equilibrium, when applied to precipitation methods, has to deal with the Solubility Product Principle. In a later chapter it will be shown how this principle is applied to the volumetric precipitation of a salt of the ion whose determination is under consideration. Suffice it to say here that, if the  $K_{s.p.}$  of the precipitated salt is too large or, in other words, if the precipitate is too soluble, equilibrium is reached too soon, the error is too large and the method is discarded at the outset.

**Standard Solutions.** Having selected a satisfactory reaction, the next consideration is to provide the reagent with which the constituent is to react. The strength of the reagent must be accurately known and not be subject to variation. If then a measured volume of the reagent is added, the exact strength of which is known, in sufficient amount to complete the reaction with the desired constituent and a means is provided of telling when the reaction is completed, we have a method of determining the weight of constituent which has reacted with the known amount of reagent. Here the Law of Definite Composition is involved since reactions always take place between weights (here expressed in grams) which are proportional to the atomic or molecular weights of



the reacting substances. In applying the Law of Definite Composition the fact that theoretically equilibrium is reached before the reaction has run absolutely to completion is ignored and the calculation is based on the assumption that the reaction is complete. We are justified in doing this because only those reactions which are substantially complete are of any use in quantitative analysis. Volumetric methods are merely indirect weighing methods in which the weight of the added reagent is ascertained by finding the volume required to supply the needed weight.

The theory of volumetric analysis and its application to calculations of data and problems of volumetric analysis will be much better understood if this type of technique is regarded as a simple method of indirect weighing.

The strength of the reagent used must be carefully determined prior to its use as the titrating solution. It is quite impossible and entirely too inaccurate to prepare the reagent from stock chemicals except in certain cases, because they are not chemically pure. The actual strength must usually be ascertained by causing an accurately known amount of a pure substance to react with the reagent in a separate titration. This procedure is known as **standardization** and, after the strength of the solution is thus determined, the reagent is spoken of as a **standard solution**. A general rule in regard to standardization is: *Standardize by a method which will, as far as possible, involve the same reactions and conditions as those used later in actual determinations.*

The standard solution must also be stable and not change its strength on standing as, otherwise, if we are not sure of the strength of the titrating solution the results of the analysis are worthless. The fact that some solutions cannot be properly standardized and others change strength from day to day places limitations on the availability of reagents which otherwise might be suitable.

The second general requirement, therefore, is the employment of stable, accurately standardized solutions which, by reacting quantitatively with the sample, give a measure of the amount of the constituent being determined.

**Indicators.** When adding the standard solution to the solution which is being titrated we must have some means of knowing definitely when an equivalent amount has been added. In the usual titration methods this is accomplished by the use of a third substance, called the **indicator**, placed either in the solution being titrated or used outside the solution, the indicator by a marked change in color or in some other property signifying that the main reaction is complete. An indicator must possess the property of not reacting with the titrating solution until the principal reaction is complete and then, on the addition of a small drop, to



manifest a sharp color change, form a precipitate or in some other way indicate that the main reaction has been satisfied. In the potentiometric titration methods, the completion of the reaction is marked by a sudden change in electrical potential.

The indicators used for precipitation methods are usually inorganic substances which form precipitates or color the solution. The indicators used in neutralization reactions are dyestuffs or related organic compounds. Starch is an ideal indicator for reactions involving iodine; the pink color of permanganate solutions serves admirably to show an excess of permanganate ions. Potassium ferricyanide, used as indicator in the dichromate method for iron, is an example of an external or "outside" indicator. Recently, indicators which change color at the equivalence points of oxidation-reduction reactions have come into use.

**End Points.** When just enough standard solution has been added, as shown by the indicator, to complete the main reaction, the **practical end point** is reached. This is the point where the indicator changes color. Strictly speaking, it is slightly in excess of the amount required for the main reaction, but the excess should not represent more than a drop or two of dilute standard solution. The practical end point must not be confused with the equilibrium point nor with the stoichiometrical point based on equivalent volumes. We must clearly distinguish between these three points, since each has a theoretical basis but in practice all three must closely coincide.

The relation between these three points can be illustrated by the titration of HCl with NaOH. The stoichiometrical (or equivalence) point in this case is that corresponding to an amount of NaOH equivalent to the HCl present, and assumes complete reaction. The equilibrium point is reached when the solution is exactly neutral and this occurs when the concentrations of  $H^+$  and  $OH^-$  are both  $1 \times 10^{-7}$ . The practical end point for the indicators usually employed in this titration is found at hydrogen-ion concentrations which are either slightly greater or less than the exact neutrality amount. It must be emphasized that the indicator must give an end point which is as near as possible to the equilibrium point and this in turn must agree closely with the stoichiometrical point.

**Accurate Measuring Vessels.** Since the accuracy of volumetric methods is so largely dependent upon the correct measuring of volumes of solution, accurately calibrated burets, pipets and flasks must be provided. The calibration should conform to the unit of volume set down by an official agency such as the Bureau of Standards. Although the unit of volume is the liter, measurements in an actual titration are made in milliliters. The procedure for calibrating volumetric apparatus and

a discussion of the fundamental unit of volume are taken up in the next section.

**Fundamental Requirements.** Summarizing the foregoing discussion, the fundamental requirements of volumetric methods are:

1. A reaction which is essentially irreversible and runs to practical completion.
2. A standardized, stable solution whose strength is accurately known and which reacts quantitatively with the substance being determined.
3. An indicator which marks the completion of the reaction.
4. Accurate measuring apparatus.

## VOLUMETRIC APPARATUS AND TECHNIQUE

The measurement of solutions in volumetric analysis is made by means of graduates, flasks, burets and pipets. For very rough measurements, measuring cylinders or graduates are used. The correctness of a volumetric analysis depends very largely on the accuracy with which volumes of solutions can be measured, consequently the greatest care must be exercised in the use of volumetric apparatus. For work demanding high precision, the apparatus must be calibrated since the graduations on the vessels may not be reliable.

**The True Liter.** The unit of volume is the liter. A true liter is the volume occupied by one kilogram of water at the temperature of its greatest density, which is approximately 4°C. A cubic centimeter is almost exactly one one-thousandth of a liter. Recent very exact determinations of the maximum density of water have placed the temperature at 3.83°C. instead of 4°C., and the one-thousandth part of a liter is in fact a trifle larger than a cubic centimeter and is called a **milliliter (ml)**. The milliliter instead of the cubic centimeter has now been adopted.

The standard temperature at which measuring vessels are used has been fixed by the Bureau of Standards at 20°C. A liter flask, for example, is usually marked to contain or to deliver at 20°C. a volume of water which at 4°C. will weigh 1000 grams *in vacuo*. The vessels may of course be calibrated and used at other temperatures, provided the calibration conforms to the above conditions.

**Flasks.** Volumetric flasks are made in capacities from 10 ml. up to 2000 ml. They are marked with an etched ring around the neck so as either *to contain* or *to deliver* the specified volume of liquid. Before a flask is used it should be cleaned with cleaning solution and rinsed with water, so that on emptying the contents a thin uniform film of water covers the inside surface. An irregular film or drops of liquid adhering



to the walls reveal insufficient cleaning; the film may distort the meniscus and the vessel will not measure accurately. A washing with ether and alcohol may be necessary to remove grease from the walls of the vessel.

Since the graduation on the flask may be in error, for very precise work a calibration should be made.

**CALIBRATION OF FLASKS.** The flask to be calibrated to contain the specified volume of liquid is cleaned, dried and weighed. The required weight of water is then calculated and the flask reweighed with this quantity of water. The following example will show how the calculation is made.

Suppose it is desired to calibrate a liter flask at the temperature of 23°C. so that it will hold a true liter of water at the standard temperature of 20°C. Obviously, it is necessary to calculate how many grams of water at 23°C. must be placed in the flask so that it will occupy a true liter when referred to 20°C.

At approximately 4°C., when weighed *in vacuo*, 1000 grams of water will occupy 1 liter. At 23°C. the density of water is 0.99756 (see table of densities in the Appendix), so that at this temperature, 997.56 grams of water will occupy 1 liter. To correct this weight *in vacuo* to the corresponding weight in air, using brass weights, the following formula is used:

$$997.56 = W_{\text{air}} + \left( \frac{1000}{1.0} - \frac{1000}{8.0} \right) 0.0012$$

from which the weight in air is found to be 996.51 grams.

The expansion of the glass flask must also be taken into consideration. The coefficient of cubical expansion of glass is 0.000026 and, since the flask is at the temperature of 23°C. instead of at 20°C., the correction is  $997.56 \times (23 - 20) \times 0.000026 = 0.08$  gram. The total weight of water to add to the flask is therefore 996.59 grams.

**Burets.** Burets are graduated tubes used for measuring volume of solutions in titrations. They are usually of 50-ml. capacity and graduated in tenths of a milliliter. The simplest type, the Mohr buret, carries a glass tip attached to the bottom of the tube by means of rubber tubing and closed with a pinchcock or with a glass bead. Glass-stoppered (Geissler) burets are preferable and must, moreover, be used in measuring oxidizing solutions.

In use, burets should first be thoroughly cleaned so that a uniform film of liquid remains on the walls when the liquid is withdrawn. Rinsing with water and then with a small volume of the solution with which the buret later is to be filled is always necessary. Burets should be filled to near the top of the graduations, that is, nearly to the zero mark.

Care must be exercised in reading a buret to place the eye on a level with the lower meniscus of the solution, so that parallax will not introduce serious errors. Further instructions and the method of reading a buret with a slotted card are given on page 51. A buret reading is estimated to one-hundredth of a milliliter, i.e., to the second decimal place.

**CALIBRATION OF BURETS.** Since the graduations on a buret do not take into account the irregularities in the bore of the tube an accurate calibration should be made. This is done by weighing the water delivered successively by the buret between the zero mark and each succeeding 5-ml. mark, until the entire capacity from zero to 50 ml. has been determined. The true volume, represented by the respective weights of water, can then be calculated and referred to 20°C. It will generally be found that the true volume delivered at each successive 5-ml. interval differs from the indicated volume, and corrections, either plus or minus, must then be applied. These corrections are best plotted on coordinate paper and pasted in the notebook.

**Pipets.** Measuring pipets are used in much the same way as burets. Transfer pipets are used to transfer single volumes of liquids. They are graduated and should be calibrated to deliver the specified volume. In filling transfer pipets the liquid is drawn into the tube to above the meniscus, the thumb is placed over the upper end and, by releasing the pressure slightly, the liquid level is allowed to fall to the mark. In allowing the solution to run into the receiving vessel, the pipet should drain for one minute and then the tip is touched to the wet inside surface of the vessel to remove the last drop; never blow through a pipet.

## THE CALCULATIONS OF VOLUMETRIC ANALYSIS

As previously indicated in a general way on page 8, the most important and most frequently used kind of calculation in quantitative analysis involves applications of the Law of Definite Composition and deals fundamentally with a direct relationship between actual weights of reacting substances and the molecular or atomic weights of the substances concerned; second in importance, and used to a lesser extent, are the calculations based on equilibrium relationships. With respect to the latter, the important applications will be discussed as they are encountered in the several types of analyses to be taken up. It is with the former type of calculation that we are here concerned.

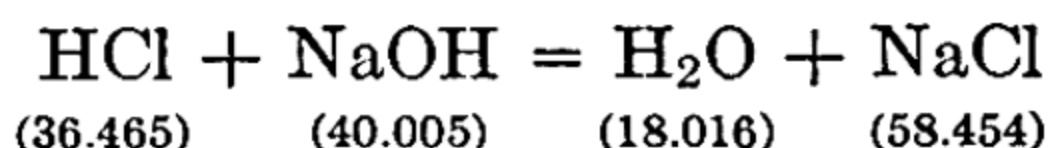
Whether a determination of a certain constituent is made by isolating and weighing a pure compound containing that constituent, as in gravimetric procedures, or whether the determination of the weight of the constituent is made indirectly by measuring the amount of reagent re-



quired for the reaction, as in volumetric procedures, the same fundamental principle applies, namely, that the weights of reacting substances bear a direct relation to their molecular or atomic weights. This is a stoichiometric relation and is expressed either as a direct proportion or as an equality of ratios.

The Law of Definite Composition not only enables us to calculate the weight of the constituent elements in a definite weight of a pure compound but it also makes possible the calculation of the weight of product formed in a reaction and the amount of substance reacting with a weighed or measured amount of reagent.

For example, the reaction between hydrochloric acid and sodium hydroxide, as represented by the molecular equation

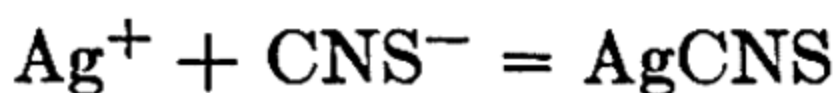


means more than the mere fact that these two substances are reacting to form water and sodium chloride. The equation states that HCl and NaOH react in the proportions of 36.465 parts by weight of HCl to 40.005 parts by weight of NaOH. Any system of weights may, of course, be used, but if gram weights are employed the equation means not only that 36.465 grams of HCl react with 40.005 grams of NaOH to form 18.016 grams of water and 58.454 grams of NaCl but also that the reaction takes place with quantities proportional to these weights.

If, therefore, it is desired to know how much NaOH is required to react with, say, 1 gram of pure HCl, the relation is a simple direct proportion which may be formulated thus:

$$\begin{array}{ccc} \text{HCl} : \text{NaOH} = 1.0000 \text{ gram HCl} : x \text{ grams NaOH.} \\ (36.465) \quad (40.005) \end{array}$$

Or, to give another example, if we wish to know how much silver is contained in a given amount of silver thiocyanate, AgCNS, which is formed by the reaction of  $\text{Ag}^+$  ions with  $\text{CNS}^-$  ions, according to the ionic equation



the calculation, in the form of a direct proportion, assumes the following form:

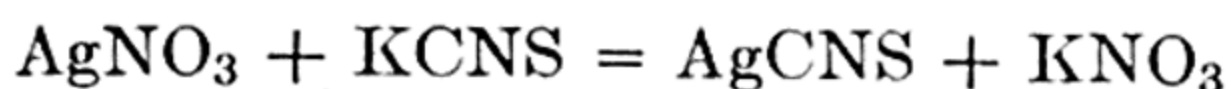
$$\begin{array}{ccc} \text{Ag} : \text{AgCNS} = \text{required wt. of Ag}(x) : \text{given wt. of AgCNS} \\ (107.880) \quad (165.948) \end{array}$$

In the form of ratios, the relationship is

$$\frac{\begin{array}{c} (\text{Ag}) \\ 107.880 \\ (\text{AgCNS}) \end{array}}{165.948} = \frac{\text{Required wt. of Ag}(x)}{\text{Given wt. of AgCNS}}$$

The ratio  $\text{Ag}/\text{AgCNS}$  gives the proportional part of Ag contained in AgCNS. If the given weight of AgCNS be taken as unity, i.e., 1.0000 gram, then the ratio  $107.880/165.948$  or  $0.6503$  is the amount of Ag in 1 gram of AgCNS.

If it is desired to know how much  $\text{AgNO}_3$  will be required to react with given amounts of KCNS according to the equation



the relation is best expressed in the form

$$\frac{\text{AgNO}_3}{\text{KCNS}} = \frac{\text{Required wt. of AgNO}_3(x)}{\text{Given wt. of KCNS}}$$

in which the ratio  $\text{AgNO}_3/\text{KCNS}$  expresses the weight of  $\text{AgNO}_3$  in grams equivalent to unit weight (1 gram) of KCNS.

Ratios of the kind illustrated are known as **chemical factors** and are extensively used in the calculations of quantitative analysis.

In the gravimetric (direct weighing) methods of analysis, we separate, purify and weigh the product of a suitably selected reaction and, from the weight of the product, calculate the weight of the constituent contained therein. In the volumetric (indirect weighing) methods, however, the final product is not weighed; the weight of constituent in the sample is calculated from the amount of reagent required to complete a suitably selected reaction involving the constituent. Moreover, the amount of reagent used is not directly weighed—but the volume, containing the required weight, is accurately measured in the titration. It therefore first becomes necessary to prepare at least one, and often two, reagents of a suitable strength and, by an accurate process of standardization, to determine the exact strength of these solutions. Then, by measuring the volume of standard solution required for the actual determination, the weight and finally the percentage of the constituent in the sample can be calculated.

Having selected, from equilibrium and practical considerations, the reaction which is most suitable for a particular determination, a convenient approximate strength of the titrating solution must be decided upon before the reagent is prepared. Several systems or units of designating strength or concentration are in use. The normal system is the most widely used. The molar system, familiar to the student from his study of equilibrium relations in his qualitative analysis course, could also be used. A method known as the titer system, in which the strength of a solution is directly given in grams per milliliter, is very simple, convenient and direct. Occasionally it is desirable to have the reagent of such a strength that each milliliter represents 1 per cent or an integral



part of 1 per cent of the reacting constituent. The normal and, to some extent, the titer systems are emphasized in the calculations in this book.

**Equivalent Weights and Normal Solutions.** A normal solution is one which contains one gram-equivalent weight of the element or compound in one liter of solution. A *gram-equivalent weight* is the number of grams of element or compound which will bring into reaction directly or indirectly 1.008 grams of hydrogen. A normal solution of an acid is one that contains 1.008 grams of replaceable hydrogen per liter of solution (more exactly 1.0080 grams, since the atomic weight of hydrogen is now placed at 1.0080); and a normal solution of a base is one that contains enough hydroxyl, namely, 17.008 grams per liter, to react with 1.008 grams of hydrogen. To prepare a 1 *N* solution of an acid, the number of replaceable hydrogens must be taken into consideration and the gram-molecular weight then divided by the proper factor, so that, in a liter of solution, there will be 1.008 grams of replaceable hydrogen. A 1 *N* solution of a base like NaOH would contain the gram-molecular weight, namely, 40.004 grams of NaOH.

A normal solution of a precipitating agent contains a weight of precipitating ion equivalent to 1.008 grams of hydrogen. The quantity of pure substance to take for the preparation of a liter of a 1 *N* solution of a precipitating solution is determined by dividing the gram-molecular weight by the valence of the precipitating ion.

In normal solutions of oxidizing and reducing reagents, the equivalent weight is determined by dividing the gram-molecular weight by the valence or electron change of the ion concerned.

A milliequivalent weight is one one-thousandth of the equivalent weight, and consequently each milliliter of a 1 *N* solution contains one gram-milliequivalent weight of the substance.

Solutions that contain two gram-equivalents per liter are 2 *N* solutions. Those containing one-half of a gram-equivalent are 0.5 *N*. The normality of solutions is usually written 2 *N*, 1 *N*, 0.5 *N*, 0.1167 *N*, etc., those less than 1 *N* being preferably expressed as decimal fractions followed by the capital letter *N*.

An advantage in using the normal system is that equal volumes of all solutions of identical normality will completely react with each other. Thus 20 ml. of 1 *N* HCl will exactly neutralize 20 ml. of 1 *N* NaOH solution. Since, however, two standard solutions are seldom of identical strength, the adjustment requiring great care and time, this advantage disappears in actual use and in calculations. As will be seen later in the detailed study of neutralization processes, the normality sometimes depends upon the kind of indicator used. The normality of a solution also depends upon the conditions under which the solution is used.

**Titers.** By the term *titer* is meant the grams of solute actually contained in a milliliter of solution or the weight of any substance which will react with or be equivalent to 1 ml. of the solution. Thus a solution of hydrochloric acid which contains, for example, 3.647 grams of pure HCl per liter, has an HCl titer of 0.003647, since this is the weight in grams contained in 1 ml. of this solution.

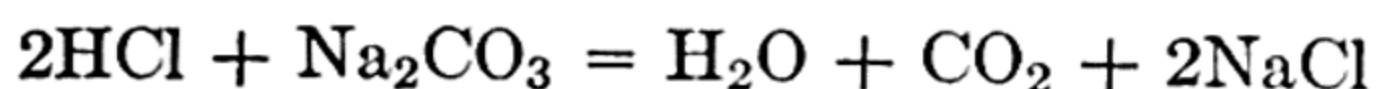
The NaOH titer of this solution may be found from the relation

$$\text{HCl} : \text{NaOH} = 0.003647 : x$$

in which  $x$  is the weight in grams of pure NaOH which can be neutralized by 1 ml. of this acid and equals 0.004000 gram. In the same manner, the  $\text{Na}_2\text{CO}_3$  titer or any other desired titer may be found by direct proportion or by use of the appropriate chemical factor.

**Calculation of the Strength of a Solution from Standardization Data.** In determining the strength of a titrating solution, either a suitable, accurately weighed amount of a pure substance is brought into reaction by titration with the necessary volume of the solution to be standardized, or else the solution is titrated with another previously standardized solution. In the first case, called a primary standardization, the data secured consist of (1) the weight of pure, primary standard and (2) the volume of solution measured from the buret; and from these data the strength of the solution is calculated.

To take a simple example, suppose that, in standardizing a solution of HCl by measuring the volume of acid required to react with a weighed amount of pure  $\text{Na}_2\text{CO}_3$  according to the reaction



it is found that exactly 30.00 ml. of the HCl solution are required to react with 0.2167 gram of pure  $\text{Na}_2\text{CO}_3$ . From these data, the appropriate titer and the normality of the HCl solution are calculated.

Since 30.00 ml. of HCl react with 0.2167 gram of  $\text{Na}_2\text{CO}_3$ , 1 ml. of the solution reacts with one-thirtieth of this weight, i.e.,  $0.2167/30.00$  or 0.007022 gram of  $\text{Na}_2\text{CO}_3$ . Each milliliter of the HCl solution therefore is equivalent to 0.007022 gram of  $\text{Na}_2\text{CO}_3$ . This is, by definition, the  $\text{Na}_2\text{CO}_3$  titer of the HCl solution, and the solution is now standardized, its strength being expressed as the value of 1 ml. in terms of  $\text{Na}_2\text{CO}_3$ .

If we wish to know the amount of solute (pure HCl) actually present in a milliliter of this solution, instead of the amount of  $\text{Na}_2\text{CO}_3$  with which 1 ml. reacts, the calculation resolves itself into simple, direct proportion:

$$\begin{array}{l} \text{Na}_2\text{CO}_3 : 2\text{HCl} = 0.007022 : x \\ (106.0) \quad (2 \times 36.47) \end{array}$$

$$M_1 V_1 = M_2 V_2 \quad 1.558$$



from which  $x = 0.004831$  gram. This is the HCl titer of the HCl solution; it means that each milliliter of the solution contains 0.004831 gram of pure solute (HCl). The chemical factor,  $2\text{HCl}/\text{Na}_2\text{CO}_3$ , might have been used instead of the direct proportion, giving, of course, the same result.

The normality of a solution may be defined as the ratio of the weight of solute actually present in a liter, a milliliter or any other volume to the weight of solute in the same volume of an exactly normal solution of the same substance. Since a normal solution is one containing one gram-equivalent weight per liter of solution, if we calculate the ratio on a liter basis, the *normality* is the ratio of the grams present to a gram-equivalent weight; if the strength per milliliter is compared, the ratio is the strength in grams per milliliter to the gram-milliequivalent weight.

In the present example, since the calculation has shown that the HCl solution contains 0.004831 gram of solute per milliliter, and a normal solution should contain the gram-milliequivalent weight, namely, 0.03647 gram per milliliter, the normality would be  $0.004831/0.03647$  or 0.1325 *N*.

But it is not necessary to know or to calculate the actual weight of solute in 1 ml. in order to calculate the normality. In fact, in the process of standardization, we experimentally determine the volume of solution required to react with a known weight of a pure substance (called the primary standard). Then, dividing the weight of pure (primary) standard by the milliliters of solution used gives the weight of standard which enters into reaction with 1 ml. of the solution. The normality may then be found directly by dividing the grams per milliliter by the gram-milliequivalent weight of the pure substance used as standard.

For the hydrochloric acid solution under discussion, it was found that 30.00 ml. of the reagent reacted with 0.2167 gram of  $\text{Na}_2\text{CO}_3$  or that 1 ml. was equivalent to 0.007022 gram of  $\text{Na}_2\text{CO}_3$ . Since an equivalent of  $\text{Na}_2\text{CO}_3$  is one-half of the molecular weight or 53, the gram-milliequivalent weight is 0.0530 gram. The normality of the acid is therefore most simply found as the ratio

$$\frac{0.007022}{0.05300} = 0.1325 \text{ } N$$

The steps in the calculation of the normality of a solution from standardization data can be combined into the single operation

$$\frac{\text{Weight of primary standard}}{\text{Volume of reagent} \times \text{gram-milliequivalent weight of the primary standard}} = \text{Normality}$$

In general, to find the normality multiply the milliliters required for the standardization by the gram-milliequivalent weight of the pure substance (standard) and divide the product into the weight of pure substance taken.

A 0.5  $N$  solution has one-half the reacting strength as a 1  $N$  solution since it contains, per liter, one-half of a gram-equivalent weight. Therefore twice the volume of a 0.5  $N$  solution would be required for reaction as for a normal solution. A very important and often used relationship follows from this. This rule can be stated thus: *Normalities are inversely proportional to volumes*. Expressed in symbols this inverse volume rule is

$$N_1 : N_2 = V_2 : V_1$$

To illustrate, if 25 ml. of a 1  $N$  solution are required for a certain reaction, then 50 ml. of a 0.5  $N$  will be needed.

For the purposes of calculation, the proportionality is best expressed as

$$V_1 N_1 = V_2 N_2$$

As a simple application of this relationship consider the following case. What volume of a 0.1500  $N$  solution will be equivalent to 30.00 ml. of a 0.1234  $N$  solution? We have here

$$\frac{30.00 \times 0.1234}{0.1500} = 24.68 \text{ ml.}$$

This relationship is by no means confined to solutions of the same solute. In fact, it is employed throughout all volumetric procedures in which two solutions are employed and particularly it is the basis of standardizing a solution and computing its normality by titration against another solution whose normality is known. In most of the volumetric procedures described in the following chapters, two solutions of opposite character are prepared and standardized, the one by a primary standardization method and the second by comparison (secondary standardization) against the first.

This application of the equivalent volume relationship by the secondary standardization of a base by means of a standard acid is shown in the following illustration. Suppose 27.25 ml. of a 0.5123  $N$  solution of  $\text{HCl}$  are found to react with 28.50 ml. of a  $\text{NaOH}$  solution. What is the normality of the  $\text{NaOH}$  solution? From the equation

$$V_{\text{HCl}} \times N_{\text{HCl}} = V_{\text{NaOH}} \times N_{\text{NaOH}}$$

we have

$$N_{\text{NaOH}} = \frac{27.25 \times 0.5123}{28.50} = 0.3144 \text{ } N$$



The ultimate objective of every quantitative determination is to find the amount of the constituent in question in the sample undergoing analysis. The calculation reduces itself to, usually, the ratio of the weight of constituent to the weight of sample, and when the result is to be expressed in terms of percentage, the computation takes the form

$$\frac{\text{Weight of pure constituent}}{\text{Weight of sample}} \times 100 = \text{Percentage}$$

In the volumetric method, the weight of constituent is obtained as the product of the volume of standard solution used and the value of 1 ml. in terms of the constituent being determined. That is

$$\text{Volume used} \times [\text{Value of 1 ml.}] = \text{Weight of constituent}$$

When the strength of the solution is expressed directly in terms of the proper titer, i.e., grams of constituent brought into reaction by 1 ml. of the titrating solution the calculation of the weight of pure constituent is then simply made on the basis of the relation

$$\text{Volume used} \times [\text{Appropriate titer}]$$

As an example, if 31.75 ml. of an HCl solution having a  $\text{Na}_2\text{CO}_3$  titer of 0.005467 are required to neutralize the  $\text{Na}_2\text{CO}_3$  contained in a sample of impure sodium carbonate the weight of pure  $\text{Na}_2\text{CO}_3$  present is

$$31.75 \times 0.005467 = 0.1735 \text{ gram}$$

On the other hand, if the strength of the titrating solution is known in terms of its normality, the weight of pure constituent is obtained by the relation

$$\text{Volume used} \times [\text{Milliequivalent weight} \times \text{Normality}]$$

To illustrate, suppose that 31.75 ml. of an HCl solution having a normality of 0.1032 are required to neutralize the  $\text{Na}_2\text{CO}_3$  contained in a sample of impure sodium carbonate, the weight of pure  $\text{Na}_2\text{CO}_3$  present is

$$31.75 \times (0.053 \times 0.1032) = 0.1735 \text{ gram}$$

the factor 0.053 being the gram-milliequivalent weight of  $\text{Na}_2\text{CO}_3$ .

The results of these two illustrations are the same, because the HCl solution having a  $\text{Na}_2\text{CO}_3$  titer of 0.005467 is a 0.1032 *N* solution.

If in the above illustrations, the weight of sample was 0.2000 gram, the proportion of pure  $\text{Na}_2\text{CO}_3$  in the sample is

$$\frac{0.1735}{0.2000} = 0.8675$$

and the percentage is 86.75.

## PROBLEM SET 2

1. Calculate the gram-equivalent weights for complete neutralization of the following acids and bases:

(a) HCl	<i>Ans.</i> (a) 36.47
(b) H <sub>2</sub> SO <sub>4</sub>	(b) 49.04
(c) NH <sub>4</sub> OH	(c) 35.05
(d) H <sub>3</sub> PO <sub>4</sub>	(d) 32.67
(e) Ba(OH) <sub>2</sub>	(e) 85.69

2. Calculate the gram-equivalent weights of the following substances:

- (a) NaCl
- (b) AgNO<sub>3</sub>
- (c) Na<sub>2</sub>CO<sub>3</sub>
- (d) BaCl<sub>2</sub>
- (e) KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>

3. What is the normality of each of the following concentrated laboratory reagents: (a) HCl (sp. gr. 1.190, containing 37.23 per cent HCl by weight); (b) NH<sub>4</sub>OH (sp. gr. 0.900, containing 28.33 per cent NH<sub>3</sub> by weight)?

*Ans.* (a) 12.15 N  
(b) 14.97 N

4. Find the normality of each of the following concentrated laboratory reagents: (a) H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84, containing 95.60 per cent H<sub>2</sub>SO<sub>4</sub> by weight); (b) HNO<sub>3</sub> (sp. gr. 1.420, containing 69.77 per cent HNO<sub>3</sub> by weight).

5. What volume of concentrated hydrochloric acid (sp. gr. 1.190 containing 37.23 per cent HCl by weight) should be taken to prepare a liter of 0.1256 N solution?

*Ans.* 10.34 ml.

6. A certain KCNS solution has a AgNO<sub>3</sub> titer of 0.1699. How much Ag could be precipitated by 35.00 ml. of this solution? What is the normality of the solution?

7. How many milliliters of 0.5 N NaOH are required to neutralize (a) 20.00 ml. of 0.5 N HCl; (b) 40.00 ml. of 0.5 N H<sub>2</sub>SO<sub>4</sub>; (c) 60.00 ml. of 0.5 N H<sub>3</sub>PO<sub>4</sub>?

*Ans.* (a) 20.00 ml.  
(b) 40.00 ml.  
(c) 60.00 ml.

8. How much Na<sub>2</sub>CO<sub>3</sub> can be neutralized by 36.25 ml. of a 0.1000 N HCl solution? How much Ag could be precipitated by this volume of acid? How many grams of KCNS would be required to precipitate the same amount of Ag as could be precipitated by 36.25 ml. of the above acid?

9. What volume of 0.1682 N NaOH solution will be neutralized by 25.00 ml. of a 0.1000 N solution of HCl? By a 0.1000 N solution of H<sub>2</sub>SO<sub>4</sub>? Why are the volumes the same?

*Ans.* 14.86 ml.

10. What volume of a 0.1342 N HCl solution will be neutralized by 0.1200 gram of NaOH? By 0.0567 gram of Na<sub>2</sub>CO<sub>3</sub>?

11. Calculate the normalities of each of the following solutions having the expressed titers:

(a) HCl (Na <sub>2</sub> CO <sub>3</sub> titer = 0.0523)	<i>Ans.</i> (a) 0.987 N
(b) Na <sub>2</sub> CO <sub>3</sub> (NaOH titer = 0.00393)	(b) 0.0981 N
(c) H <sub>2</sub> SO <sub>4</sub> (H <sub>2</sub> SO <sub>4</sub> titer = 0.00486)	(c) 0.0991 N
(d) KOH (H <sub>2</sub> SO <sub>4</sub> titer = 0.0985)	(d) 2.008 N



## VOLUMETRIC ANALYSIS

12. If 27.52 ml. of an HCl solution will neutralize 28.50 ml. of an NaOH solution, what volume of HCl will be neutralized by 1 ml. of the NaOH? If the acid solution has a normality of 0.5000, what is the normality of the base?

13. What volume of a 0.500 *N* solution of  $\text{Na}_2\text{CO}_3$  is equivalent to 35.0 ml. of an acid solution whose normality is 0.100 *N*? *Ans.* 7.00 ml.

14. In titrating 20.50 ml. of KOH solution, 22.45 ml. of a 0.5000 *N* solution of  $\text{H}_2\text{SO}_4$  were used. Calculate the weight in grams of KOH which reacted.

15. If a certain acid solution had a normality of 0.1432 what is its (a) NaOH titer; (b)  $\text{Na}_2\text{CO}_3$  titer; (c) HCl titer? *Ans.* (a) 0.005728  
(b) 0.007590  
(c) 0.005222

16. Calculate the weight of (a) NaOH neutralized if a titration required 30.00 ml. of a 0.1 *N* solution of an acid; (b) if a sample of  $\text{NaHCO}_3$  required the same volume of the acid.

17. Calculate the value of 1 ml. of each of the following:

- |  |                         |
|--|-------------------------|
| (a) 0.2650 <i>N</i> $\text{Na}_2\text{CO}_3$ | <i>Ans.</i> (a) 0.01405 |
| (b) 0.5000 <i>N</i> $\text{H}_2\text{SO}_4$  | (b) 0.02452             |
| (c) 0.0100 <i>N</i> NaOH                     | (c) 0.004000            |
| (d) 0.0500 <i>N</i> $\text{Ba}(\text{OH})_2$ | (d) 0.004285            |

18. If 15.0 ml. of concentrated HCl (sp. gr. 1.19, containing 37.23 per cent pure HCl) is diluted to a liter what is the (a) normality, (b) the HCl titer of the solution?

19. If 25.00 ml. of an HCl solution having a  $\text{Na}_2\text{CO}_3$  titer of 0.005165 reacts with 30.00 ml. of an NaOH solution what is the normality of the base? *Ans.* 0.08121 *N*

20. Calculate the percentage of pure  $\text{Na}_2\text{CO}_3$  in a sample of an alkaline substance if a 1.5000-gram sample required 35.00 ml. of a 0.1 *N* solution of HCl for titration.

## CHAPTER III

### NEUTRALIZATION METHODS

#### GENERAL LABORATORY INSTRUCTIONS

**Preliminary Preparations.** Upon being assigned a desk, check the equipment against the list furnished. Examine each piece of glassware for chipped edges, scratched bottoms and other defects. Make sure all items are present and in good condition; report shortages and defects to instructor or supply room.

Each item should have its proper place in the desk and be returned at the close of laboratory periods to its appointed location. Glassware should be kept separate from ironware. Never return dirty apparatus to the desk. Before leaving the laboratory, wipe off the desk top with sponge and towel. Make sure your desk is locked before leaving.

Cleaning reagent is to be used for burets, pipets and flasks; all other apparatus is cleaned with soap and brush. Before attending to other preparations listed below, make 500 ml. of dichromate cleaning solution according to the following directions:

Dissolve 50 grams of commercial  $\text{Na}_2\text{Cr}_2\text{O}_7$  in 150 ml. of water, warming the solution to effect more rapid dissolving. Cool, pour into a large evaporating dish, and add slowly, while stirring constantly, 230 ml. of concentrated  $\text{H}_2\text{SO}_4$ ; use commercial sulfuric acid if available. When the mixture has cooled, at the end of the laboratory period transfer to a 500-ml. wide-mouthed bottle. Use this cleaning reagent only for flasks, burets and pipets.

While the cleaning solution is cooling, procure some glass tubing and make a wash bottle, according to the design and type recommended by the instructor. A simple type is shown in Fig. 2.

Cut three 8-inch lengths of glass rod and fire-polish the ends. These will be used as stirring rods.

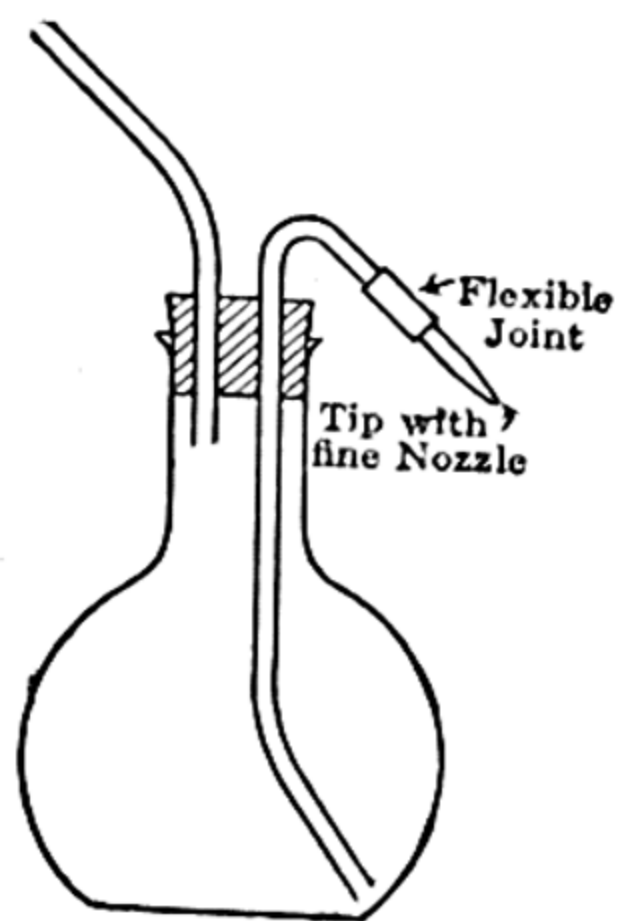


FIG. 2. Wash bottle.



Place some calcium chloride in the bottom compartment of the desiccator. Place a thin coating of vaseline on the ground joint between vessel and cover. Desiccators are used to store dried samples, crucibles, etc.

**Exercises with the Analytical Balance.** Reread those portions of Chapter I which deal with the use and care of the balance. Go to the balance assigned; study its construction and operation. Familiarize yourself with the weights in the weight box.

Determine the rest point of the empty balance. If not in satisfactory adjustment, call the instructor; do not attempt the adjustment yourself.

Of the several different methods of carrying out a weighing operation, two are here described. The first and simplest of all is by equal swings; the other is known as the sensitivity method. The instructor will specify the method of weighing which is to be used in the course.

1. **METHOD OF EQUAL SWINGS.** Place an empty, clean and dry weighing bottle or crucible on the left-hand pan, after the point of rest has been determined. Then place the 5-gram weight on the right-hand pan; release beam and pan support; the pointer will probably move more rapidly to the right, showing that the object weighs more than 5 grams. Add the 2-gram weight; if too heavy, replace by the 1-gram weight. A single deflection of the pointer to right or left is sufficient to decide whether the object is lighter or heavier than 5 grams. Let us assume that the weight of the object is between 6 and 7 grams, as determined by the brass weights.

Now begin with the fractional weights. First try the 0.5-gram (500 milligrams), then the 200-milligram and so on down to the 10-milligram weight. Suppose the weight now is established as 6.73.

The next two units, namely, the milligrams and tenths of milligrams, must now be determined by the rider on the beam scale. Close the balance case and place the rider on the 5-milligram division of the beam. If too heavy, move it to 2.5, otherwise to 7.5. Again subdivide the beam scale by a third setting of the rider. Finally, a fourth setting will probably be necessary to equalize definitely the loads between weight and object. It is only during the last two or three settings of the rider that the pointer swings need be observed carefully and the swings of the pointer in both directions definitely noted. If final equilibrium is determined with rider at 4.5, the correct weight of the object is 6.7345.

Although this method is more easily understood and performed by the beginning student, the sensitivity method furnishes the better training.

2. **SENSITIVITY METHOD OF WEIGHING.** As already defined, by sensitivity is meant the number of pointer scale divisions through which the point of rest is moved by an excess load of 1 milligram. First determine



the rest point of the balance; suppose it is 0.3 scale divisions to the left of center.

Then proceed to counterbalance a clean, dry weighing bottle or crucible until the fractional weights are exhausted. Then determine the two positions, with the rider, between which the true weight lies. Suppose that the weight load is 6.73 and that the rider at the 5-milligram position is too great and at the 4-milligram too little, the true weight being between 6.7340 and 6.7350.

Determine the sensitivity for this load by finding the points of rest for both loads, by averaging swings to left and right, in both cases. Take the difference between these two new positions of the pointer. Suppose that, with the rider on 4 milligrams, the new point of rest is at 1.5 on right and with the rider at 5 milligrams the new rest point is at 2.1 on the left. This gives a sensitivity of 3.6 scale divisions.

The position where the rider would have been placed, between 4 and 5 milligrams, in order to equalize the balance and bring the point of rest back to 0.3 is now calculated. Since the pointer rest position is moved through 3.6 scale divisions for an extra load of 1 milligram, in order to bring the pointer to the original rest point of 0.3 it must be moved through  $1.5 + 0.3$  or 1.8 scale divisions. To move the pointer rest position 1.8 scale divisions to the left, there must be added  $1.8/3.6$  or 0.5 milligram (0.0005 gram). The weight of the object is therefore 6.7345 grams.

**Methods of Weighing Samples.** There are in general two methods of weighing samples. In the one method, the sample, dried to remove moisture unless otherwise directed, is placed in a weighing bottle; the bottle with its contents is accurately weighed; portions of approximately the desired weight are transferred to beakers or flasks for dissolving; and finally the weighing bottle with remainder of sample is reweighed. The difference in weight is the portion of sample taken for analysis. The most convenient and certain means of transferring the sample from the weighing bottle is to fashion a small spoon or ladle-like tool from thin sheet aluminum. The transfer spoon should be short enough to fit into the weighing bottle when the cover is in place; it is kept in the bottle and weighed with the sample.

Another method of weighing samples, though less desirable, is to weigh out onto a weighed watch glass or weighing scoop the desired portion of sample. For exact work tared watch glasses are used to correct for buoyancy. Care must of course be taken not to spill sample on the balance pan. The weighed sample is then brushed with a camel's hair brush into the dissolving beaker or flask.

Instructions will be given in the procedures or by the instructor as to the specific method to be employed.



**Determination of Moisture in a Sample.** Clean two weighing bottles and their stoppers. Attach to each a small sticker with your initials. Number the bottles "1" and "2." Dry them with stoppers placed in a slanting position for 1 hour in the drying oven at  $105^{\circ}\text{C}.$ ; remove to desiccator, allow to cool to room temperature, place stoppers in the bottles and weigh accurately. Repeat the drying of the empty bottles until the successive weights do not differ by more than 0.2 milligram.

Transfer into the weighing bottles 1 to 2 grams of the sample issued for this determination, stopper the bottles tightly and weigh accurately. The increase in the weight is the weight of sample.

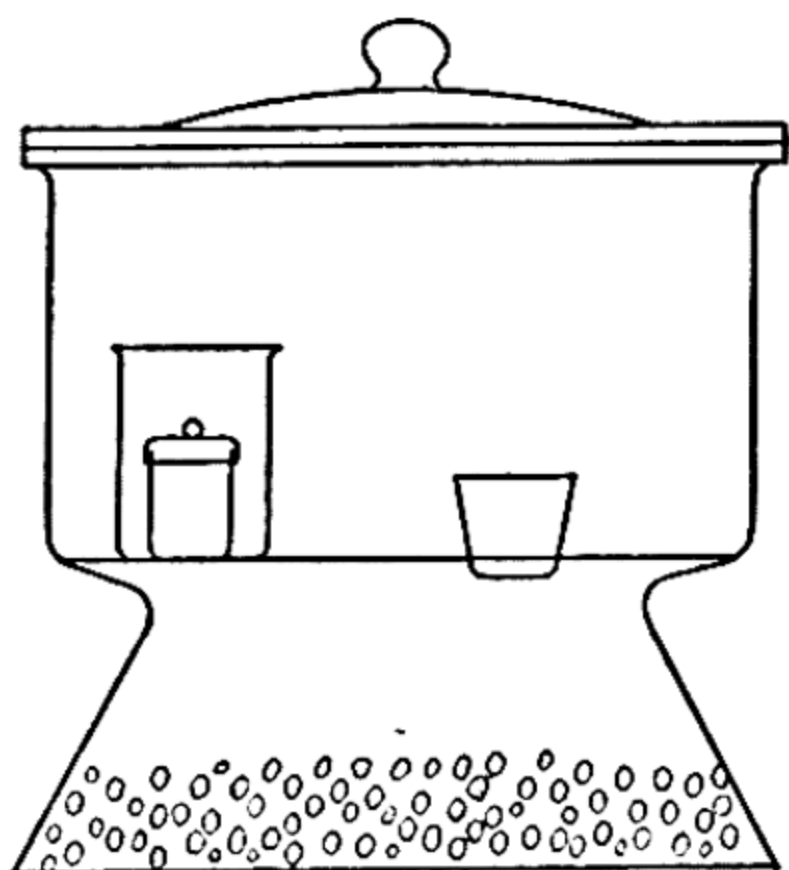


FIG. 3. Desiccator.

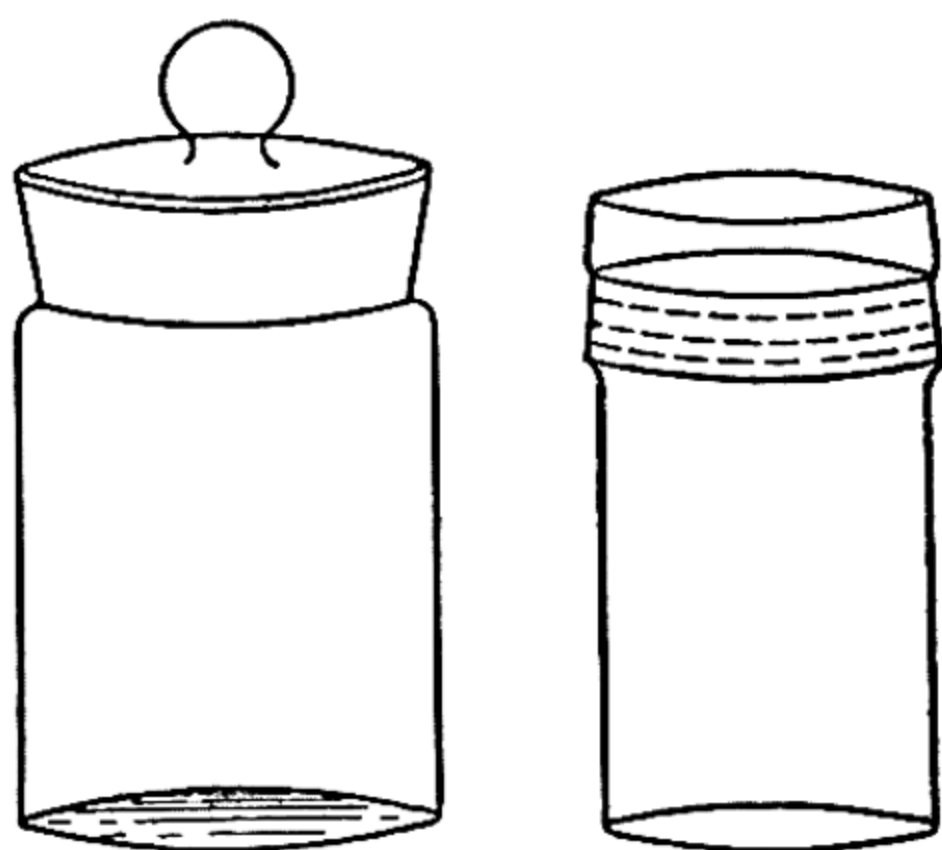


FIG. 4. Weighing bottles.

Return the weighing bottles to the drying oven, place stoppers in a slanting position, allow samples to remain there for at least 1 hour (2 hours or overnight is better). Remove from oven, stopper the bottles, cool in desiccator and weigh. Reheat and repeat the other operations. The loss in weight of the sample is the moisture removed by drying. This divided by the weight of sample and multiplied by 100 is the percentage of moisture.

### GENERAL CONSIDERATIONS OF ACIDIMETRY AND ALKALIMETRY

The measurement of the acid strength of a substance, by titration with a standard solution of a base, is termed acidimetry. Conversely, alkalimetry is the determination of the basic strength of a material by titration with a standard acid solution. Both processes employ neutralization reactions. By these methods practically all acids and bases and many salts of weak acids and bases are analyzed.

For the preparation of standard acids, we are practically limited to hydrochloric, sulfuric and nitric acid, of which the first named is most frequently used. For bases, sodium hydroxide is most generally selected,

although potassium hydroxide and barium hydroxide are occasionally employed. In strength they vary between 0.5 *N* and 0.05 *N*, an approximately 0.1 *N* solution being, in most cases, the most desirable strength.

Since these reagents cannot be obtained in a pure form, solutions made from them must be standardized against pure primary standards. As standards, for hydrochloric acid, pure  $\text{Na}_2\text{CO}_3$  is generally employed and, in case an independent primary standardization of sodium hydroxide is desired, pure potassium acid phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ , is an excellent standard.

It is highly important that the correct indicator be used for acid-base titrations. There are many organic dyestuffs which can be employed, because they have the property of changing color over definite narrow ranges of hydrogen-ion concentration; the indicator chosen is the one which changes color at the hydrogen-ion concentration at which the reaction comes to equilibrium. The two indicators which will be employed in the following experiments are (modified) methyl orange and phenolphthalein. The latter is colorless in solutions having a hydrogen-ion concentration greater than about  $10^{-8}$  and pink in solutions of  $10^{-9}$  or less. Ordinary methyl orange is pink or red in rather strongly acid solutions (hydrogen-ion concentration of  $10^{-3}$ ) and orange in somewhat less acidic solutions. Because the color change for ordinary methyl orange is hard for beginners to distinguish in 0.1 *N* solutions, this indicator is modified by the addition of another dye, xylene cyanole FF, which shows a reddish color at a hydrogen-ion concentration of about  $10^{-3}$ , passes through a gray transition range and is green at  $10^{-5}$ . The preparation of these indicator solutions is given in the list of indicators in the Appendix.

For the titration of strong acids with strong bases either indicator may be employed. Phenolphthalein is used for the titration of weak acids; it cannot well be used in precise work for titrations with bases which contain carbonates. Methyl orange or, better still, methyl red is used for ammonia titrations.

For precise work, an indicator blank should be run. This is the volume of standard reagent necessary to affect the indicator in those titrations in which the equivalence point does not coincide with the hydrogen-ion concentration at which the indicator changes color.

## DETERMINATIONS OF ALKALINITY AND ACIDITY

Practical application of neutralization reactions is made in the following experimental work in the determination of the alkaline strength of



samples of impure sodium carbonate, and of the acid strength of potassium acid phthalate or, alternatively, oxalic acid. Required for such volumetric determinations are standard solutions of HCl and NaOH; the preparation and standardization of these reagents follow.

#### PREPARATION AND STANDARDIZATION OF APPROXIMATELY 0.1 N SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE

**Calculations and Preparation.** A normal solution of an acid contains 1.008 grams of replaceable hydrogen per liter of solution. A liter of hydrochloric acid of normal strength contains 36.465 grams of pure hydrogen chloride since in this weight of solute there are 1.008 grams of replaceable hydrogen. Since a solution of approximately 0.1 N strength is best suited for the following procedures, 0.1 of a gram-mole of HCl must be used. This requires  $0.1 \times 36.465$  or 3.65 grams. The reagent from which this is obtained is concentrated hydrochloric acid, of specific gravity of 1.19 and containing 37.3 per cent of pure HCl. Each milliliter of this solution contains  $1.19 \times 0.3723$  or 0.443 grams of pure HCl. To furnish 3.65 grams requires therefore  $3.65/0.443$  or 8.2 ml.

For the solution measure out about 8.5 ml. of concentrated hydrochloric acid, dilute with about 200 ml. of distilled water, transfer to the clean liter measuring flask and fill to the mark with distilled water. Keep the solution in a liter bottle. Label the bottle "approximately 0.1 N HCl" and place your name on the label.

A normal solution of NaOH should contain 40.005 grams of replaceable hydroxyl per liter, and this amount is contained in a gram-molecular weight, 40.005 grams. For a 0.1 N solution, one-tenth of a gram-mole is required, that is, 4.0005 grams per liter. Since sodium hydroxide is not pure, weigh out on the rough balance about 4.2 grams of NaOH and dissolve in about 200 ml. of distilled water. Pour this solution into a liter measuring flask. Add distilled water until about half full; shake thoroughly and then fill the flask to the mark with distilled water. Transfer the NaOH solution to a bottle provided with a rubber stopper instead of a glass one because NaOH will cement a ground-glass stopper to the bottle. Label the bottle properly.

**Comparison of Solutions.** Place the burets in the buret clamp on the stand and fill both with dichromate cleaning reagent, allowing the solution to remain in them for a little while. Remove the cleaning agent, rinse out with water and grease the stopcocks with a thin layer of stopcock grease. Fill with water and note whether they leak.

Prepare two meniscus reading cards, one for each buret. This is done

Handwritten notes:  $1.19 \times 0.3723 = 0.443$

Handwritten notes:  $36.465 \times 0.1 = 3.6465$



by making two horizontal cuts, about one-half inch apart and two inches long, in a small flexible cardboard. The area below the lower cut is then blackened by inking with a pen. The card is slid onto the buret, with the black area placed at a level so that the top of the inked portion is about 1 millimeter below the bottom of the meniscus of the liquid in the buret. Fig. 5 shows such a card.

When all is in readiness, rinse one of the burets with a few milliliters of the HCl solution and the other with the NaOH solution. After rinsing, fill the burets with HCl and NaOH solutions and bring the solutions within the graduations, being careful that air bubbles are not trapped below the stopcock. Adjust the reading card; record the readings of the two burets; estimate to the second decimal place.

After taking the readings, run out into a clean 250-ml. Erlenmeyer flask 35 ml. of the HCl solution, using the left hand to manipulate the stopcock. Add 50 ml. of distilled water and two drops of modified methyl orange indicator. Run in NaOH solution with constant swirling of the flask with the right hand until the pink color has given place to a green.

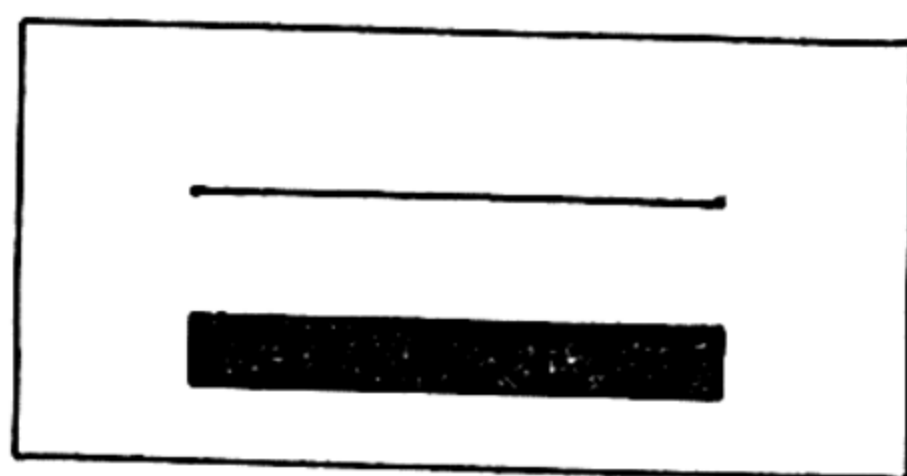


FIG. 5. Buret reading card.

Add HCl solution dropwise until the pink color is again restored; continue these additions until one drop of NaOH will change the color of the solution to a faint green and one drop of HCl will color the solution a faint pink. In titrating always choose the faintest color as an end point; also treat each portion in the same manner; thus if you stop on a faint pink end point here do likewise in subsequent titrations. Record the final buret readings. If the volumes used differ by more than 5 ml., add water to the bottle containing the stronger solution and repeat the trial comparison.

Refill the burets and make another comparison titration, using approximately the same volumes as before. Make a third comparison and then calculate the equivalent volume ratios as illustrated below.

**Calculations.** Suppose that on comparing these two solutions one of the titrations showed that 32.61 ml. of NaOH reacted with 33.75 ml. of HCl. Then, since 32.61 ml. of NaOH are equivalent to ( $\approx$ ) 33.75 ml. of HCl,

$$1 \text{ ml. of NaOH} \approx \frac{33.75}{32.61} \approx 1.035 \text{ ml. of HCl}$$

and, conversely,

$$1 \text{ ml. of HCl} \approx \frac{32.61}{33.75} \approx 0.966 \text{ ml. of NaOH}$$

Handwritten calculations:

$$\begin{array}{r} 33.75 \\ \times 1.035 \\ \hline 36.468 \end{array}$$

1.035



In this manner, compute the ratios for the several comparison titrations, rejecting those that do not agree closely and averaging the remainder. Submit the calculations to the instructor for criticism. If acceptable results are not obtained, carry out more comparison titrations. These equivalent-volume ratios will be used not only in correcting total volumes used later in standardization of the HCl solution, but also for computing the strength of the NaOH solution.

In this first series of titrations, the student will experience little difficulty in securing checking results. Agreement of the ratios within 2 to 3 parts per thousand is satisfactory.

**Standardization of HCl Solution with Pure  $\text{Na}_2\text{CO}_3$ .** Of the several possible ways of standardizing a solution of HCl, the direct titration against weighed portions of pure  $\text{Na}_2\text{CO}_3$  as outlined below is recommended. Aside from the high accuracy of the method, it has the advantage here that in the subsequent analysis of soda ash (impure sodium carbonate), to which use this reagent is to be put, the same conditions and reactions are involved. Hydrochloric acid solutions may of course be standardized against a previously standardized solution of a base if one is available. The strength may also be determined gravimetrically by precipitation as AgCl, and it is possible to obtain by distillation of HCl solutions a constant boiling mixture, in which the percentage of HCl by weight is 20.22 (at a barometric pressure of 760 millimeters Hg).

**OUTLINE OF METHOD OF STANDARDIZATION.** Portions of pure  $\text{Na}_2\text{CO}_3$  are weighed and dissolved. Methyl orange indicator is added and the solutions are titrated with HCl. Adjustment of the end point is made with the NaOH solution which has previously been compared with the HCl. Pure  $\text{Na}_2\text{CO}_3$  especially made for standardization purposes may readily be purchased, or it may be prepared in the laboratory by heating  $\text{NaHCO}_3$  to a temperature of  $270^\circ$  to  $300^\circ\text{C}$ . for 1 hour. In case it becomes necessary to prepare pure  $\text{Na}_2\text{CO}_3$  from sodium bicarbonate, proceed as follows. Place an iron crucible on a triangle resting on an iron ring. Place within this crucible another triangle, and insert into the triangle a porcelain crucible containing about 6 grams of  $\text{NaHCO}_3$ ; adjust the triangle so that the porcelain crucible is wholly within the iron crucible and an air space exists between the walls of the two crucibles. Suspend a  $350^\circ\text{C}$ . thermometer in the  $\text{NaHCO}_3$  so that the bulb is covered. Heat the iron crucible with a small flame at first and gradually increase the heat until  $270^\circ\text{C}$ . is reached. During this time occasionally stir the  $\text{NaHCO}_3$ . Heat very slowly from  $270^\circ$  to  $300^\circ\text{C}$ . so that one hour elapses during this interval. Do not allow the temperature to rise above  $300^\circ\text{C}$ . Transfer the crucible and  $\text{Na}_2\text{CO}_3$  to a desiccator, allow to cool, then

transfer to a weighing bottle, stopper well and keep in the desiccator until ready for use.

**PROCEDURE.** Weigh accurately into three numbered 250-ml. Erlenmeyer flasks three portions of  $\text{Na}_2\text{CO}_3$ , previously dried at  $140^\circ\text{C}$ ., of about 0.2000 gram each.

Dissolve each portion in 80 ml. of water. Fill clean burets with HCl and NaOH and take the initial readings, being sure that no air bubbles are in the tip below the stopcock. Add 2 drops of modified methyl orange indicator to the flask containing the smallest weight of  $\text{Na}_2\text{CO}_3$ . Run in HCl, with constant stirring, until a faint pink coloration is obtained, and then run in NaOH until a faint green or gray appears. Adjust the end point after this fashion until a point is reached where one drop of acid or one drop of base will change the color of the solution. Record the final buret readings and repeat the standardization with the other two carbonate standards.

**CALCULATIONS.** (1) *Strength of the HCl Solution.* Let us suppose that in neutralizing 0.1620 gram of pure  $\text{Na}_2\text{CO}_3$ , 2.00 ml. of the NaOH and 32.07 ml. of the HCl solutions were required for complete neutralization. Then, since, as shown by the example illustrating comparison, 1 ml. of NaOH is equivalent to 1.035 ml. of HCl, the volume of HCl used by the NaOH is  $2.00 \times 1.035$  or 2.07 ml. The net volume of HCl, namely, that used by the  $\text{Na}_2\text{CO}_3$  alone, is  $32.07 - 2.07$  or exactly 30.00 ml. If the titration required 30.00 ml. of HCl to neutralize 0.1620 gram of pure  $\text{Na}_2\text{CO}_3$ , 1 ml. of the HCl will have neutralized 0.1620 gram/30.00 ml. or 0.005400 gram of  $\text{Na}_2\text{CO}_3$ . This, by definition, is the  $\text{Na}_2\text{CO}_3$  titer of the HCl solution.

Since the normality is, by definition, the ratio of the concentration compared to an exactly normal solution, the normality is found by dividing the weight of solute or its equivalent per milliliter by the gram-milliequivalent weight. Each milliliter of the HCl solution is equivalent to  $0.1620/30.00$  or 0.005400 gram of  $\text{Na}_2\text{CO}_3$ , as found by direct titration. The gram-equivalent weight of  $\text{Na}_2\text{CO}_3$  is  $\text{Na}_2\text{CO}_3/2$  or 53.00 grams; the gram-milliequivalent weight is therefore  $53.00/1000$  or 0.05300 gram. Then the normality is

$$\frac{0.005400}{0.05300} = 0.1019 N$$

These steps may be combined into the single equation

$$\frac{0.1620}{30.00 \times 0.05300} = 0.1019 N$$



Calculate, as shown in this example, the normality of the HCl separately for each standardization. The results should agree within two parts per thousand; the deviations are thus a measure of the precision of the standardization. If satisfactory results are not obtained, the standardization must be repeated.

Close agreement in the normality obtained by the several runs generally indicates, as well, that the standardization has been correctly carried out. But this is not necessarily true because, although all like operations were performed in exactly the same manner, a serious constant error could have been repeatedly introduced. Good precision does not always guarantee high accuracy. Failure of agreement in the standardization values is generally due to carelessness and inexperience and the students' lack of appreciation of the care that must be exercised. A repetition of the standardization generally results in a more satisfactory agreement of results. If results do not agree on the set of titrations, the standardization must, of course, be repeated.

(2) *Strength of the NaOH Solution.* From the equivalent volume ratio obtained from comparison data, together with the normality of the HCl solution, the normality of the NaOH solution is readily computed. For example, if 32.61 ml. of NaOH were found to react with 33.75 ml. of HCl, the NaOH solution is 1.035 times stronger than the HCl solution. Since the strength of the HCl, in the above example, is 0.1019 *N*, the normality of the NaOH is  $0.1019 \times 1.035$  or 0.1054 *N*. Use might also be made of the relation

$$\begin{aligned}V_{\text{HCl}} \times N_{\text{HCl}} &= V_{\text{NaOH}} \times N_{\text{NaOH}} \\33.75 \times 0.1019 &= 32.61 \times x \\x &= 0.1054 \text{ } N\end{aligned}$$

Compute the normality of the NaOH solution by multiplying the normality of the HCl solution by the number of milliliters of HCl neutralized by 1 ml. of the NaOH.

#### DETERMINATION OF THE ALKALINE STRENGTH OF SODA ASH

Soda ash is crude sodium carbonate and contains small amounts of sodium bicarbonate together with impurities. The  $\text{NaHCO}_3$  contributes to the total basicity of the sample. In reporting results it is customary to report the total alkaline strength as percentage of  $\text{Na}_2\text{CO}_3$ .

**Procedure.** Spread the sample issued you on a clock glass, attach a label with your name and place in a drying oven, at  $140^\circ\text{C}$ ., for one hour; this is done to remove moisture from the sample. Then transfer the dried sample to a weighing bottle and place in the desiccator.

The method of securing a uniform sample in this determination consists in taking aliquot portions of the dissolved, weighed sample as described below.

Weigh out accurately a sample of the dried soda ash of about 1 gram into a 200-ml. beaker. Add 50 ml. of distilled water to dissolve the sample. Transfer the solution to a 250-ml. measuring flask, wash out the beaker and add distilled water from the wash bottle until the lowest part of the meniscus is level with the graduation. Rinse out a 50-ml. pipet with some of this solution, thoroughly shake the sample in the flask and then pipet 50 ml. into a 250-ml. Erlenmeyer flask. Add 30 ml. of water and two drops of modified methyl orange indicator. With HCl and NaOH in readiness in burets, add HCl, while swirling constantly, until a faint pink is reached; then alternately add NaOH and HCl to adjust the end point. Repeat the determination with two other 50-ml. portions of the sample.

**Calculations.** When methyl orange is used as indicator, both of the alkaline constituents in the sample are shown to have been neutralized by the acid at the point of color change. The total basicity may therefore be computed from the net volume of HCl used and expressed as a percentage in terms of the equivalent of  $\text{Na}_2\text{CO}_3$ . To illustrate, suppose that in the titration of an aliquot portion (one-fifth of a 1.0000-gram sample) there were employed a total volume of 28.00 ml. of a 0.1019 *N* solution of HCl and, for back titration, 2.60 ml. of NaOH, 1 ml. of which is equivalent to 1.035 ml. of the HCl. Each milliliter of 0.1019 *N* HCl reacts with  $0.053 \times 0.1019$  or 0.005400 gram of  $\text{Na}_2\text{CO}_3$  (or its equivalent of  $\text{NaHCO}_3$ ) in the sample. The net volume of HCl used was  $28.00 - (2.60 \times 1.035)$  or 25.32 ml. Therefore, the weight of basic constituents in the sample, expressed as grams of  $\text{Na}_2\text{CO}_3$ , is

$$25.32 \times 0.005400 = 0.1367 \text{ gram}$$

The percentage of  $\text{Na}_2\text{CO}_3$  in a 0.2000-gram portion of the sample is therefore

$$\frac{0.1367}{0.2000} \times 100 = 68.35 \text{ per cent}$$

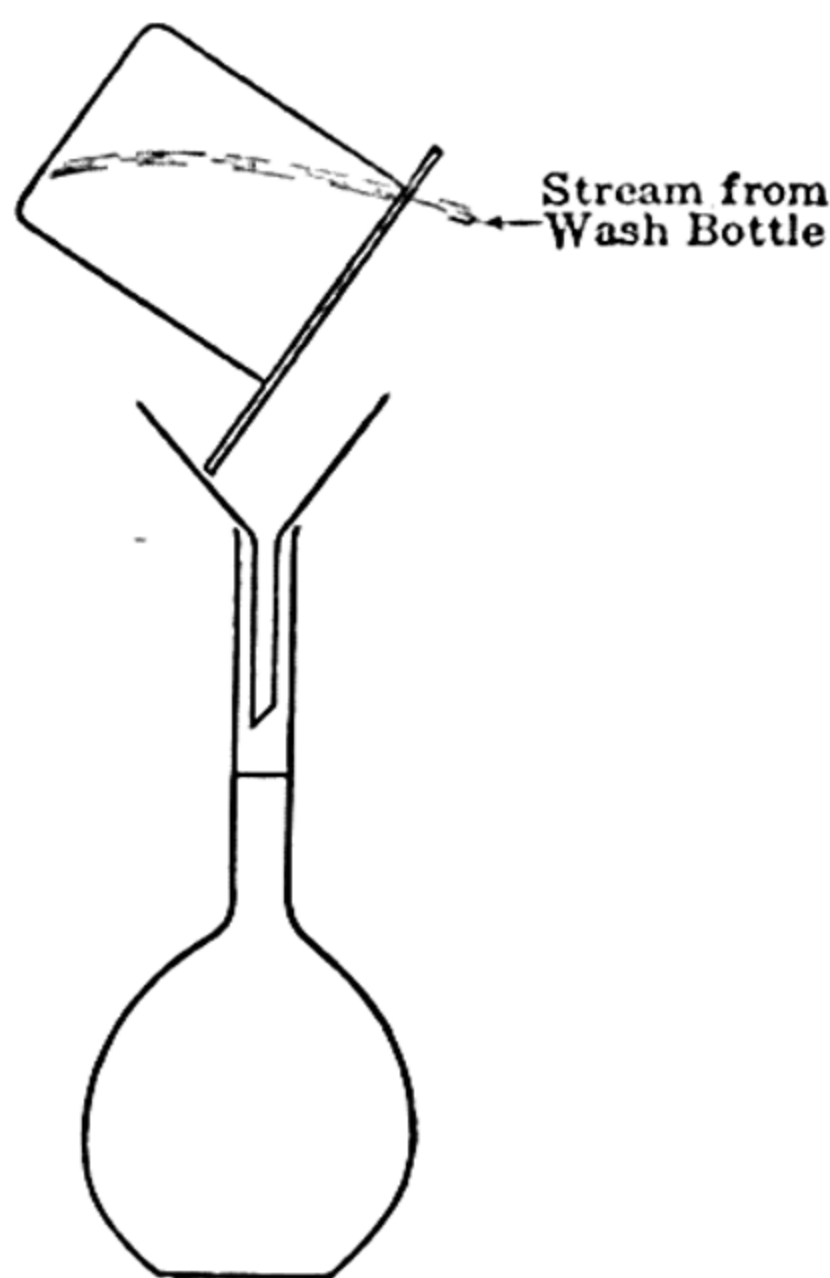


FIG. 6. Transfer of liquid to flask.



These steps can be consolidated into the single set of mathematical operations

$$\frac{25.32 \times 0.1019 \times 0.05300}{0.2000} \times 100 = 68.35 \text{ per cent}$$

In the way illustrated, calculate for each of the titrations the net volume of HCl used. Multiply this by the normality of the HCl solution and by the milliequivalent weight of  $\text{Na}_2\text{CO}_3$ . Divide the product by one-fifth of the weight of the sample and multiply by 100. The result is the total alkalinity of the sample, expressed as percentage of  $\text{Na}_2\text{CO}_3$ .

Results which check within two to three parts per thousand are very good. Submit calculations and results, as recorded in the record book, to the instructor. If results are not acceptable, the experiment must be repeated.

Not every beginner is entirely successful with this, his first volumetric analysis. A large discrepancy may be due to faulty standardization (even though the normality checked), to careless weighing, to incorrect sampling, to errors in reading burets, etc. Sometimes, even, the error is discovered in the computations. Minor errors creep into the analysis through the use of uncalibrated burets, pipet and flask and weights, end-point errors, temperature variations, etc. If a re-run must be made, all the sources of error should be guarded against and minimized wherever possible.

#### DETERMINATION OF THE ACID STRENGTH OF POTASSIUM ACID PHTHALATE

Potassium acid phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ , is phthalic acid,  $\text{H}_2\text{C}_8\text{H}_4\text{O}_4$ , in which one of the hydrogen atoms has been replaced by potassium. It behaves as a weakly ionized monobasic acid. It is an excellent primary standard, widely used for the standardization of solutions of strong bases such as NaOH. Samples of the impure salt will be used as an exercise in the following determination.

**Standardization of NaOH Solution.** Although the NaOH to be used has already been standardized by comparison with HCl of a known strength, it is here suggested that an independent standardization of the base be made with pure potassium acid phthalate.

Weigh accurately three portions of about 0.8 gram each of the standard into 250-ml. Erlenmeyer flasks. Add 80 ml. of distilled water to each flask and heat to boiling. Cool, add two drops of phenolphthalein indicator and titrate without delay with the NaOH solution to a pink color end point.

**CALCULATIONS.** The molecular weight of potassium acid phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ , is 204.2, hence the milliequivalent is 0.2042 gram. Ascertain from the instructor (or otherwise) the purity of the standard and correct the weight of the portions used. Divide this corrected weight by the net volume of  $\text{NaOH}$  used; this will give the amount of pure  $\text{KHC}_8\text{H}_4\text{O}_4$  which reacted with 1 ml. of the base. To find the normality divide this titer value by 0.2042. Results should not deviate by more than one or two parts per thousand.

**Determination.** Dry the issued sample of impure potassium acid phthalate for one hour in an oven maintained at  $120^\circ\text{C}$ . Transfer to a weighing bottle and place in desiccator. Weigh into 300-ml. Erlenmeyer flasks three separate portions of approximately 1 gram each. Dissolve the smallest weighed sample with about 80 ml. of distilled water, heat to boiling, cool to room temperature under the water tap, add two drops of phenolphthalein indicator and add without delay from the buret the standard base until the solution changes from colorless to a light pink. Repeat with the other samples, being careful to go slowly when the volume of base reaches that used by the first sample.

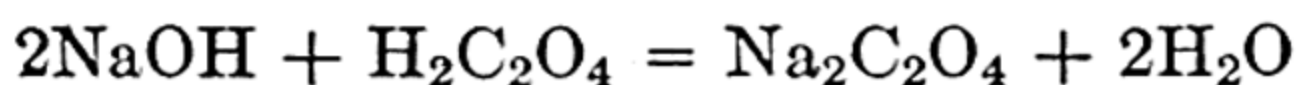
**CALCULATIONS.** Multiply the volume of  $\text{NaOH}$  used by its normality and in turn by the milliequivalent weight of  $\text{KHC}_8\text{H}_4\text{O}_4$  (0.2042), divide this product by the weight of the sample and multiply by 100. This will give the percentage purity of the sample in terms of pure potassium acid phthalate. Percentages should agree within several parts per thousand. Have the instructor approve data and calculations before making out the final report.

#### DETERMINATION OF THE STRENGTH OF AN OXALIC ACID SOLUTION

**Outline of Method.** The solution of oxalic acid submitted as an unknown is diluted, phenolphthalein is added and the solution is titrated with standard  $\text{NaOH}$  to a faint pink. The pink is just discharged with standard  $\text{HCl}$ , after which the solution is boiled. If no color appears the titration is completed with the standard  $\text{NaOH}$  in the hot solution.

Phenolphthalein indicator is sensitive to weak acids and is especially valuable in the titration of organic acids. At high dilutions it loses its sensitivity as an indicator.

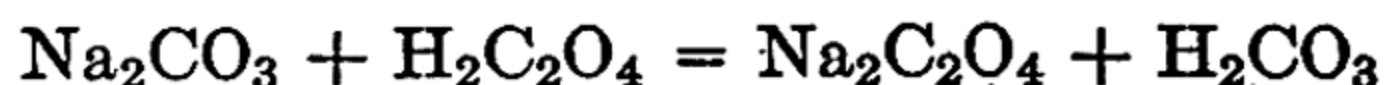
The reaction involved in the titration of oxalic acid is



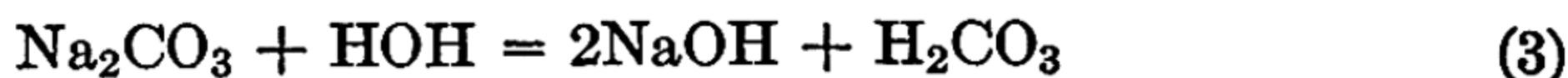
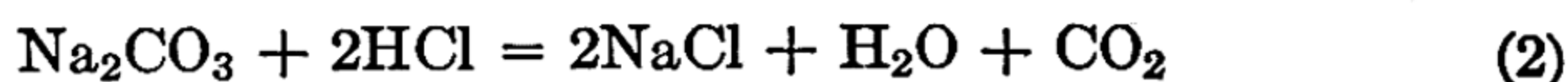
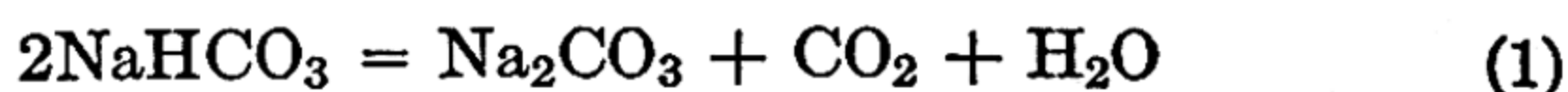
After the discharge of the pink coloration with  $\text{HCl}$  the solution is



boiled. NaOH generally contains some  $\text{Na}_2\text{CO}_3$ , and this gives rise to the formation of  $\text{NaHCO}_3$



Since  $\text{NaHCO}_3$  does not furnish enough  $\text{OH}^-$  ion to cause phenolphthalein to remain pink, evidently all the NaOH solution added will not be effective in the titration. However, after boiling the solution,  $\text{Na}_2\text{CO}_3$  is formed; this reacts with the HCl, and if the  $\text{Na}_2\text{CO}_3$  is in excess it will hydrolyze sufficiently to give a return of the pink coloration. The reactions involved are



The  $\text{OH}^-$  ions due to (3) will cause a return of the pink coloration.

**Procedure.** Measure out 20 ml. of the oxalic acid solution and dilute to 50 ml. with distilled water. Add two drops of phenolphthalein indicator, stir and run in the standard NaOH solution until the colorless solution turns pink. Carefully discharge the color with standard HCl and add a few drops in excess. Boil the solution for about three minutes. Should the pink coloration return, add acid as before and boil again for three minutes. If no color reappears, bring it back with the NaOH, add acid, a drop or two in excess, and boil as before. Complete the titration in a hot solution. If no color reappears on boiling, choose as an end point the faintest pink color which lasts about one minute. Note that in this titration the change is from colorless to colored. This is the most accurate way of judging end points. Repeat the above titration with another 20-ml. portion of oxalic acid.

From the volumes of standard solutions used and the volume of oxalic acid sample neutralized, compute the normality of the oxalic acid solution.

### QUESTIONS

1. In general, what acids are used for the preparation of standard solutions? Can nitric acid be used under all circumstances? What substances might you use for preparation of a standard acid solution without the necessity of a standardization titration? How could you prepare a solution of HCl as a standard solution without a standardization titration?

2. What substances are available for the preparation of standard base solutions? Could one use  $\text{Ba}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ , KOH,  $\text{NH}_4\text{OH}$ ? If not, why?

3. What pure substances are available for the standardization of acid solutions? For basic solutions? Distinguish between primary and secondary standardization.

4. Why use methyl orange in the standardization of HCl? Could phenolphthalein be used as well? When must phenolphthalein be used as indicator? What indicator would you employ for the titration of  $\text{NH}_4\text{OH}$  with HCl? (See section on indicator theory.)

5. What advantages and disadvantages are there in using aliquot portions of the sample of soda ash?

6. Summarize the errors which might account for poor results obtained in determining the alkalinity of soda ash.

7. Do the same as in 6 for the potassium acid phthalate or oxalic acid sample.

8. How might errors be avoided or corrected (1) in taking aliquot portions, (2) in reading the burets, (3) in the use of indicators?

9. Summarize, with examples, the various types of chemical compounds which may be analyzed by acid or base titrations.

### STOICHIOMETRIC CALCULATIONS OF NEUTRALIZATION

Calculations involving the data of acidimetry and alkalimetry may conveniently be arranged, for purposes of assignment and study, under the following three heads:

1. Normalities, titers, standardization, etc.
2. Adjustment of solutions.
3. Mixed alkali calculations.

Illustrations have already been given, in both Chapter II and the foregoing procedures, showing the preparation, comparison and standardization of solutions and computation of percentage of constituents. Additional illustrations, in the form of problems relating to data of this kind as well as involving weight of primary standard and weight of sample and supplying further applications of acid-base determinations, are given below in Problem Set 3.

Calculations involving the adjustment of the strength of solutions as well as mixed alkali titrations are discussed on page 91 and followed by Problem Set 5. Calculations of  $p\text{H}$  values and titration curves are illustrated beginning with page 61 and followed by Problem Set 4.

### PROBLEM SET 3

#### ACID-BASE CALCULATIONS

1. What weight of pure solute is required for the preparation of liter quantities of 0.5000  $N$  solutions of the following reagents?

- (a)  $\text{HC}_2\text{H}_3\text{O}_2$
- (b)  $\text{H}_2\text{SO}_4$
- (c) KOH
- (d)  $\text{Ba}(\text{OH})_2$

*Ans.* (a) 30.03 grams  
(b) 24.52 grams  
(c) 28.05 grams  
(d) 42.85 grams



2. What volume of "concentrated" hydrochloric acid solution (sp. gr. 1.190, containing 37.23 per cent of HCl by weight) must be taken for the preparation of a liter of 0.5000 *N* HCl?

3. If 32.56 ml. of a 0.1382 *N* HCl solution were found, on comparison, to react with 31.85 ml. of an NaOH solution, what is the normality of the base?

*Ans.* 0.1413 *N*

4. A certain acid solution has a normality of 0.1652. How many milliliters of 0.1267 *N* NaOH are required for the neutralization of 35.00 ml. of the acid?

5. A titration of 30.00 ml. of a certain HCl solution required 35.80 ml. of a solution of NaOH. What is (a) the value of 1 ml. of the HCl in terms of NaOH, and (b) the value of 1 ml. of the NaOH in terms of HCl?

*Ans.* (a) 1.19

(b) 0.838

6. A solution was made by dissolving 6.0 grams of NaOH, adding 5 ml. of HCl (sp. gr. 1.19, 37.23 per cent HCl by weight) and diluting to a liter. What was the normality of this solution?

7. Calculate the  $\text{Na}_2\text{CO}_3$  titer for each of the following solutions:

(a) 0.1847 *N* HCl

*Ans.* (a) 0.00979

(b) 0.2000 *N* NaOH

(b) 0.01060

(c) 0.1000 *N*  $\text{H}_2\text{SO}_4$

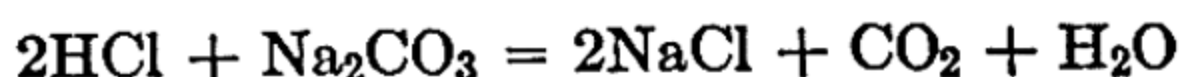
(c) 0.005300

8. A sodium hydroxide solution was standardized directly against pure potassium acid oxalate,  $\text{KHC}_2\text{O}_4$ . If 0.5321 gram of the  $\text{KHC}_2\text{O}_4$  were used and required 30.00 ml. of the sodium hydroxide solution, what was the normality of the solution?

9. What weight of pure  $\text{Na}_2\text{CO}_3$  would you use to standardize an approximately 0.2 *N* solution of HCl so that not more than 35 ml. of the acid is to be used?

*Ans.* 0.37 gram

10. In standardizing a hydrochloric acid solution it was found that 27.50 ml. of the acid completely neutralized 0.1456 gram of pure  $\text{Na}_2\text{CO}_3$  according to the reaction



What is (a) the  $\text{Na}_2\text{CO}_3$  titer of the solution; (b) the HCl titer of the HCl solution; (c) the normality of the solution?

11. Exactly 30.00 ml. of an NaOH solution was found to require 15.5 ml. of 0.2 *N* HCl plus 29.0 ml. of 0.1 *N*  $\text{H}_2\text{SO}_4$  for neutralization. What was the normality of the NaOH solution?

*Ans.* 0.2 *N*

12. A KOH solution was standardized with pure potassium acid phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ , using 0.7530 gram of the standard and 42.67 ml. of the base. Calculate the normality of the KOH solution.

13. (a) Calculate the normality of a hydrochloric acid solution having a specific gravity of 1.120. (b) What is the normality of a sulfuric acid solution containing 48.00 per cent of  $\text{H}_2\text{SO}_4$  by weight?

*Ans.* (a) 7.316 *N*

(b) 13.51 *N*

14. Calculate the percentage purity of sodium hydroxide pellets, a 1.0000-gram sample of which required for neutralization 48.10 ml. of 0.5 *N*  $\text{H}_2\text{SO}_4$ .

15. An analysis of soda ash furnished the following data: weight of sample, 5.0000 grams; using  $\frac{1}{5}$  aliquots required 37.50 ml. of 0.1320 *N* HCl and 2.35 ml. of NaOH solution, 1 ml. of the latter being equivalent to 1.22 ml. of the acid. Calculate the percentage of the  $\text{Na}_2\text{CO}_3$  in the sample.

*Ans.* 24.23 per cent

16. Calculate the percentage of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , in a 1.0000-gram sample if 26.51 ml. of a 0.1167 *N* sodium hydroxide solution was used in the determination.

17. In determining combined nitrogen by the Kjeldahl method, the sample is digested with sulfuric acid which converts the nitrogen to  $\text{NH}_3$ . The latter is displaced with strong  $\text{NaOH}$  and distilled into a measured excess of standard acid. The excess is then determined by titration with a standard base.

If in such an analysis, 50.00 ml. of 0.500  $N$  acid is employed and for back-titration 40.00 ml. of 0.550  $N$  base is used, what weight of  $N$  was present in the sample?

*Ans.* 0.0420 gram

18. A 25-ml. sample of vinegar (assume density of 1) required 41.60 ml. of 0.6000  $N$   $\text{NaOH}$  for titration. Calculate the percentage of  $\text{HC}_2\text{H}_3\text{O}_2$  in the sample.

19. Phosphorus in steel is determined by oxidizing the ferric phosphide to  $\text{H}_3\text{PO}_4$ , precipitating this as  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$  and treating the ammonium phosphomolybdate with a measured excess of standard base, and finally back-titrating with standard acid. In the dissolving reaction 23 $\text{NaOH}$  are equivalent to 1 $P$ , therefore the gram-milliequivalent weight of phosphorus is  $30.98 \div 23000$  or 0.001347.

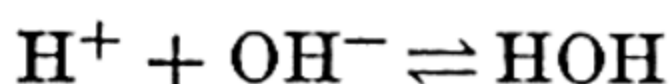
If in such a determination, a 2-gram sample of steel, upon proper treatment according to the above steps, required 20.00 ml. of 0.1085  $N$   $\text{NaOH}$  and 17.50 ml. of 0.09862  $N$   $\text{HNO}_3$ , what was the percentage of phosphorus in the steel?

*Ans.* 0.030 per cent

20. In standardizing an  $\text{HCl}$  solution, it was found necessary, in order to neutralize 27.65 ml. of the  $\text{HCl}$  solution, to use 18.50 ml. of  $\text{NaOH}$  solution, the  $\text{HCl}$  titer of which was 0.03567, and 6.50 ml. of another  $\text{NaOH}$  solution having an  $\text{HCl}$  titer of 0.03456. What was the  $\text{HCl}$  titer of the  $\text{HCl}$  solution?

## THE THEORY OF NEUTRALIZATION

**Equilibrium of the Ions of Water.** The fundamental reaction of all neutralization reactions is the union of hydrogen ions and hydroxyl ions, leading to the formation of water, as represented by the ionic reaction



When equilibrium is reached, the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  in equilibrium with non-ionized  $\text{HOH}$  can be evaluated. Water, considered as a very weak electrolyte, ionizes to a slight extent into  $\text{H}^+$  ions and  $\text{OH}^-$  ions. The ionization constant for water is expressed by the equation

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{HOH}}} = K_{\text{ion}}$$

Since, however, the concentration of the non-ionized  $\text{HOH}$  is practically constant and is enormous compared to the concentration of its ions, the equilibrium expression can be simplified by rewriting it in the form

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_{\text{ion}} \times C_{\text{HOH}} = K_w = 1.2 \times 10^{-14}$$

which shows that the product of the concentrations of the ions is equal to a constant,  $K_w$ , which, at 25°C., has the value  $1.2 \times 10^{-14}$ .



This relationship is of fundamental importance in the study of neutralization reactions, for it shows that in any aqueous solution, no matter whether it is an acid, a base, a salt solution or water itself, the product of the gram-ion concentrations of  $H^+$  and  $OH^-$  is always constant. A liter of pure water, since it ionizes to the same extent into  $H^+$  ions and  $OH^-$  ions, contains at room temperature approximately  $1 \times 10^{-7}$  gram-ion of hydrogen and an equal concentration of  $OH^-$  ions. It is, by definition, neutral.

By definition an **acidic solution** is one which contains an *excess of hydrogen ions*, and a **basic solution** is one which contains an *excess of hydroxyl ions*. A **neutral solution** is one which contains *equal concentrations* of these two ions. In fact, it is impossible to have any aqueous solution whatsoever in which there are not both hydrogen and hydroxyl ions. It follows, from the water equilibrium which demands concentrations such that  $C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$ , that if the concentration of one set of ions—say that of hydrogen ions—is known, the concentration of the other set becomes fixed.

It is customary to designate solutions with respect to their acidity or basicity by their hydrogen-ion concentration. A neutral solution is one having a hydrogen-ion concentration of approximately  $1 \times 10^{-7}$ , that is, one containing 0.0000001 gram-ion of hydrogen ion per liter of solution. This value is significant in that it constitutes the dividing line between acids and bases. The character of any solution may be designated by writing the hydrogen-ion concentration in decimal form as 0.00001, or in exponential form as  $1 \times 10^{-5}$ , or in terms of what is known as the *pH* value.

### *pH* VALUES

Designating the acidity or basicity of a solution by means of its *pH* value arose from the following considerations. A very accurate means of determining the hydrogen-ion concentration of a solution is to measure the electromotive force which is set up in an electrolytic cell between a hydrogen electrode (a platinum electrode coated with platinum black and saturated with hydrogen gas) dipping into a solution which is normal with respect to  $H^+$  ions and a hydrogen electrode dipping into the solution whose hydrogen-ion concentration is desired. (See Fig. 10 on page 88.) The formula, a modification of the Nernst equation, which relates the electromotive force of the cell with the hydrogen-ion concentration, is

$$\text{e.m.f.} = 0.059 \log \frac{1}{C_{H^+}}$$

in which 0.059 is a constant, 1 the concentration of  $H^+$  ions in the normal (standard or reference) electrode and  $C_{H^+}$  the concentration of  $H^+$  ions in the second electrode. By measuring the e.m.f., the factor,  $\log 1/C_{H^+}$ , can be calculated. The term  $pH$  is merely a substitution for the factor,  $\log 1/C_{H^+}$ , and accordingly is defined as the **logarithm of the reciprocal of the hydrogen-ion concentration**. Thus, if the  $C_{H^+}$  is  $1 \times 10^{-5}$  the  $pH$  is 5, or if  $C_{H^+}$  is  $1 \times 10^{-10.36}$  the  $pH$  is 10.36.

The calculation of the  $pH$  value from a given value of  $C_{H^+}$  is a simple matter. If, for example, a certain acidic solution is known to have a  $C_{H^+}$  of  $1 \times 10^{-4}$ , the conversion to  $pH$  is based on the relationship

$$\begin{aligned} pH &= \log \left( \frac{1}{1 \times 10^{-4}} \right) \\ &= \log 1 - \log (10^{-4}) \\ &= 0 - (-4) \\ &= 4 \end{aligned}$$

Note that the  $pH$  is merely the exponential value of the hydrogen-ion concentration with the negative sign removed. This, indeed, is a fortunate mathematical relationship, converting the hydrogen-ion concentration to the  $pH$  scale by simply expressing the exponent of the logarithmic relation as a positive number.

Another example: What is the  $pH$  value of a solution whose hydrogen-ion concentration is  $1 \times 10^{-8.75}$ ?

$$\begin{aligned} pH &= \log \frac{1}{1 \times 10^{-8.75}} \\ &= 0 - (-8.75) \\ &= 8.75 \end{aligned}$$

The calculation is somewhat more complicated when the value of  $C_{H^+}$  is expressed as a mixed number, as in the following example.

Calculate the  $pH$  of a solution having a  $C_{H^+}$  of  $2.6 \times 10^{-4}$ .

$$\begin{aligned} pH &= \log \frac{1}{C_{H^+}} \\ &= \log \left( \frac{1}{2.6 \times 10^{-4}} \right) \\ &= \log 1 - \log 2.6 \times 10^{-4} \\ &= 0 - (\log 2.6 \times 10^{-4}) \end{aligned}$$



It now becomes necessary to convert the coefficient 2.6 into a logarithm, in order to incorporate it as part of the exponent. The logarithm of 2.6 is +0.41. Therefore

$$\begin{aligned} 2.6 \times 10^{-4} &= 1.0 \times 10^{-4+0.41} \\ &= 1.0 \times 10^{-3.59} \end{aligned}$$

Then

$$\begin{aligned} pH &= 0 - (\log 10^{-3.59}) \\ &= 0 - (-3.59) \\ &= 3.59 \end{aligned}$$

In a manner analogous to the designation of  $C_{H^+}$  values in terms of pH scale, we might express hydroxyl-ion concentrations on a similar logarithmic scale. That is

$$pOH = \log \frac{1}{C_{OH^-}}$$

It is to be noted in particular that, as the numerical value of pH increases, the  $H^+$ -ion concentration decreases. pH values up to 7 design-

TABLE II

Solution	Percentage Ionization	$C_{H^+}$	pH	$C_{OH^-}$
1.0 N HCl	79.6	$1 \times 10^{-0.1}$	0.1	$1 \times 10^{-13.9}$
0.1 N HCl	94.8	$1 \times 10^{-1.02}$	1.02	$1 \times 10^{-12.98}$
0.01 N HCl	99.8	$1 \times 10^{-2}$	2.0	$1 \times 10^{-12}$
0.0001 N HCl	100.0	$1 \times 10^{-4}$	4.0	$1 \times 10^{-10}$
0.000001 N HCl	100.0	$1 \times 10^{-6}$	6.0	$1 \times 10^{-8}$
HOH (pure water)	0.062	$1 \times 10^{-7}$	7.0	$1 \times 10^{-7}$
0.000001 N NaOH	100.0	$1 \times 10^{-8}$	8.0	$1 \times 10^{-6}$
0.0001 N NaOH	100.0	$1 \times 10^{-10}$	10.0	$1 \times 10^{-4}$
0.01 N NaOH	99.5	$1 \times 10^{-12}$	12.0	$1 \times 10^{-2}$
0.1 N NaOH	92.9	$1 \times 10^{-12.97}$	12.97	$1 \times 10^{-1.03}$
1.0 N NaOH	76.6	$1 \times 10^{-13.88}$	13.88	$1 \times 10^{-0.12}$

nate solutions which are acidic; a pH of 7 is an exactly neutral solution; and pH values greater than 7 refer to basic solutions, since in solutions which are basic the hydrogen-ion concentration must have some value less than  $10^{-7}$ .

Table II gives the hydrogen- and hydroxyl-ion concentrations and the pH values for HCl and NaOH solutions of the specified concentrations, calculated from the relation

$$C_{H^+} \times C_{OH^-} = 1 \times 10^{-14}$$

The existing (or actual) hydrogen-ion concentration of a solution, expressed either in terms of  $C_{H^+}$  or in terms of the pH value, must not be

TABLE III  
IONIZATION CONSTANTS AND PERCENTAGE IONIZATION

Electrolyte	Equilibrium Ratio	$K_{ion}$	Percentage Ionization for 0.1 N Solutions
HCl	$C_{H^+} \times C_{Cl^-} \div C_{HCl}$	(1.0)	94.8
HNO <sub>3</sub>	$C_{H^+} \times C_{NO_3^-} \div C_{HNO_3}$	(1.0)	92.0
H <sub>2</sub> SO <sub>4</sub>	$C_{H^+} \times C_{HSO_4^-} \div C_{H_2SO_4}$	(1.0)	90.0
	$C_{H^+} \times C_{SO_4^{2-}} \div C_{HSO_4^-}$	(0.03)	60.0
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$C_{H^+} \times C_{HC_2O_4^-} \div C_{H_2C_2O_4}$	0.038	40.0
	$C_{H^+} \times C_{C_2O_4^{2-}} \div C_{HC_2O_4^-}$	0.00005	1.0
H <sub>3</sub> PO <sub>4</sub>	$C_{H^+} \div C_{H_2PO_4^-} \div C_{H_3PO_4}$	0.01	27.0
	$C_{H^+} \times C_{HPO_4^{2-}} \div C_{H_2PO_4^-}$	0.062	0.1
	$C_{H^+} \times C_{PO_4^{3-}} \div C_{HPO_4^{2-}}$	0.0124	0.0001
HNO <sub>2</sub>	$C_{H^+} \times C_{NO_2^-} \div C_{HNO_2}$	0.0005	8.0
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	$C_{H^+} \times C_{C_2H_3O_2^-} \div C_{HC_2H_3O_2}$	0.000018	1.34
H <sub>2</sub> CO <sub>3</sub>	$C_{H^+} \times C_{HCO_3^-} \div C_{H_2CO_3}$	0.063	0.12
	$C_{H^+} \times C_{CO_3^{2-}} \div C_{HCO_3^-}$	0.0106	0.0017
HCN	$C_{H^+} \times C_{CN^-} \div C_{HCN}$	0.097	0.01
H <sub>2</sub> S	$C_{H^+} \times C_{HS^-} \div C_{H_2S}$	0.079	0.05
	$C_{H^+} \times C_{S^{2-}} \div C_{HS^-}$	0.0141	0.0001
	$(C_{H^+})^2 \times C_{S^{2-}}$	0.02211	
NaOH	$C_{Na^+} \times C_{OH^-} \div C_{NaOH}$	(1.0)	92.9
Ca(OH) <sub>2</sub>	$C_{Ca^{++}} \times (C_{OH^-})^2 \div C_{Ca(OH)_2}$	0.03	75.0
NH <sub>4</sub> OH	$C_{NH_4^+} \times C_{OH^-} \div C_{NH_4OH} + C_{NH_3}$	0.000018	1.31
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>			77.9
NH <sub>4</sub> Cl			85.3
NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>			80.0

confused with the total available acid strength of the solution. In other words, the  $H^+$ -ion concentration which may be present at any moment depends upon the concentration of the solution and its degree of ionization, whereas the total amount, which becomes available during neutralization, is a measure of the total acidity of the solution. Thus, a liter



of normal HCl and a liter of normal  $\text{HC}_2\text{H}_3\text{O}_2$  both have the same available amount of hydrogen ion (1.008 grams or 1 gram-ion), since both require an equivalent amount of a base for neutralization, but the actual hydrogen-ion concentration of a normal solution of HCl is nearly one hundred times greater than the hydrogen-ion concentration of a normal  $\text{HC}_2\text{H}_3\text{O}_2$  solution, since the former is a strongly ionized acid and the latter a weak acid in which the  $\text{H}^+$ -ion concentration is low. In a titration for the determination of total acidity it is of little consequence whether the acid being titrated is a strong or weak acid, in so far as total hydrogen-ion concentration is concerned, since as hydrogen ions are removed more of the non-ionized molecules will dissociate. How such a titration is conducted is, however, of great importance.

Table III gives the degree of ionization and the ionization constants of a number of acids, bases and salts at room temperature.

### NEUTRALIZATION AND HYDROLYSIS

Since the fundamental reaction which takes place when acids and bases interact is the union of  $\text{H}^+$  ions and  $\text{OH}^-$  ions to form water, neutralization means that the water equilibrium is involved, the value of  $K_w$  must be satisfied and equilibrium, as expressed by the relation

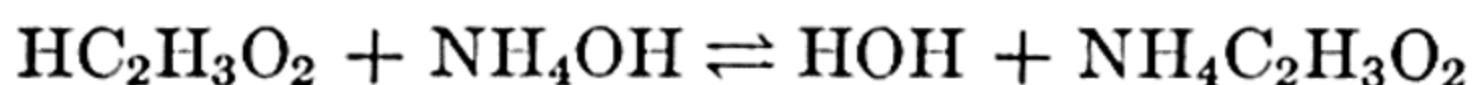
$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_w = 1.2 \times 10^{-14}$$

must be maintained. When equivalent quantities of an acid and base are mixed the final equilibrium is not necessarily at neutrality. Indeed, it is only for those pairs of acids and bases for which the extent of ionization is the same that final equilibrium comes at neutrality ( $\text{pH}$  of 7); all other pairs, when reacting in equivalent amounts, reach final equilibrium in the mixed solutions in either the acidic or basic region, that is, at  $\text{pH}$  values smaller or greater than 7. The final equilibrium point reached in an acid-alkali titration depends upon the nature of the salt formed in the reaction, and this, in turn, depends upon the degree of ionization of the acid and base interacting.

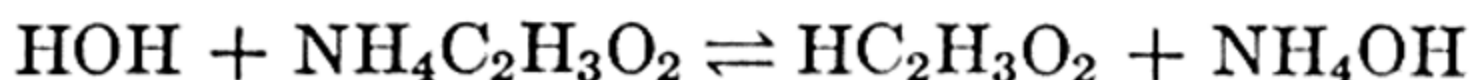
It is highly important to know at what  $\text{pH}$  value final equilibrium is reached, when equivalent quantities of reacting acids and bases are brought together in a titration in order that the proper indicator be selected.

In order to understand why equilibrium at the equivalence point in a titration does not always come at strict neutrality, the possibility and extent of hydrolysis of the salt resulting from the reaction must be considered. Hydrolysis may be defined as the reaction of the ions of water with the ions of salts which are formed from weakly ionized acids or

bases. A hydrolysis reaction is the reverse of a neutralization reaction; in fact, in the reversible reaction between an acid and a base it is the interaction of the products of this reaction. To illustrate, when  $\text{HC}_2\text{H}_3\text{O}_2$  reacts with  $\text{NH}_4\text{OH}$



the ions of water react with the ions of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$



to reform certain definite amounts of  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NH}_4\text{OH}$ . If more non-ionized  $\text{HC}_2\text{H}_3\text{O}_2$  should form than non-ionized  $\text{NH}_4\text{OH}$ , more  $\text{H}^+$  ions are used up than  $\text{OH}^-$  ions, and the solution would then be basic. In this particular case, as shown later, the amounts of both happen to be almost the same, resulting in a solution which is practically neutral.

Hydrolysis is the reaction of  $\text{H}^+$  ions or  $\text{OH}^-$  ions with the anions or cations of weakly ionized acids or bases. It can be regarded as the reverse of a neutralization reaction, since the ions of the salt produced react with hydrogen or hydroxyl ions to reform the original acid or base. The degree to which the acid and base ionize, that is, whether they are weak or strong electrolytes, determines the extent to which hydrolysis will take place. The behavior, point of equilibrium and titration requirements of four typical pairs of acids and bases are discussed below.

**Potentiometric and Indicator Titrations.** There are, as pointed out on page 31, two methods by which a titration can be conducted with respect to the location of the end point. Both methods can be applied to acidimetric and alkalimetric, as well as oxidation and reduction and precipitation reactions. The older and common method is to use indicators which give a sharp color change when the equilibrium point of the reaction is reached, and the selection of the correct indicator depends upon knowing this equilibrium point. In acid-base titrations, when indicators are used, the nature of the acid or base being titrated furnishes the guide for the selection of the indicator. A potentiometric titration (see page 87) consists in measuring the changes in the electromotive force of an electrolytic cell made up of the combination of a standard reference electrode and another electrode which is put into the solution being neutralized. As the reaction gradually runs to completion by the addition of measured quantities of the standard reagent, there will be corresponding changes in the voltage of the cell. In the case of an acid-base titration, a potentiometric titration consists, in fact, of a series of hydrogen-ion concentration measurements, as described on page 88, so that, when titrating an acid by a standard solution of base, the hydrogen-ion concentration gradually and then rapidly decreases.



The change in the voltage of the cell is so rapid in the vicinity of the equilibrium point that an experienced analyst judges the end point by the abnormally large deflection of the voltmeter needle of the potentiometer. By actually recording the voltages, as the neutralization progresses and from the Nernst equation for the hydrogen electrode,

$$\text{e.m.f.} = 0.059 \log \frac{1}{C_{\text{H}^+}}$$

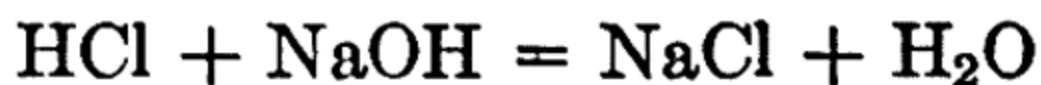
the hydrogen-ion concentrations or, better still, the  $p\text{H}$  values directly can be calculated from the relation

$$\frac{\text{e.m.f.}}{0.059} = \log \frac{1}{C_{\text{H}^+}} = p\text{H}$$

A series of  $p\text{H}$  values is thus obtained. When these values are plotted on coordinate paper against added volumes of standard reagent, a graph is obtained similar to the ones illustrated in a later section. Such graphs are known as titration curves. The equivalence point and therefore the end point can then be more accurately located from the curve. The vertical portion of such a curve gives the range over which the hydrogen-ion concentration or  $p\text{H}$  is undergoing the most rapid change, and the bisection point of the vertical portion (the inflection point) locates the definite equilibrium point and is taken as the end point.

Curves which show graphically the changes taking place during the addition of successive volumes of reagent can also be plotted by calculation from proper data. Curves of this kind are of considerable value in following the course of a reaction and in finding the end point in an actual titration. Such calculated curves, which are followed more or less closely in a potentiometric titration and give a general idea of the changes in an indicator titration, are shown for typical combinations of acids and bases.

**Reaction between Strong Acids and Strong Bases.** The first case to consider is the neutralization of a strong acid, such as  $\text{HCl}$ , by a strong base such as  $\text{NaOH}$ . Suppose that 1 gram-mole of  $\text{HCl}$  is allowed to react with 1 gram-mole of the  $\text{NaOH}$ . According to the reaction

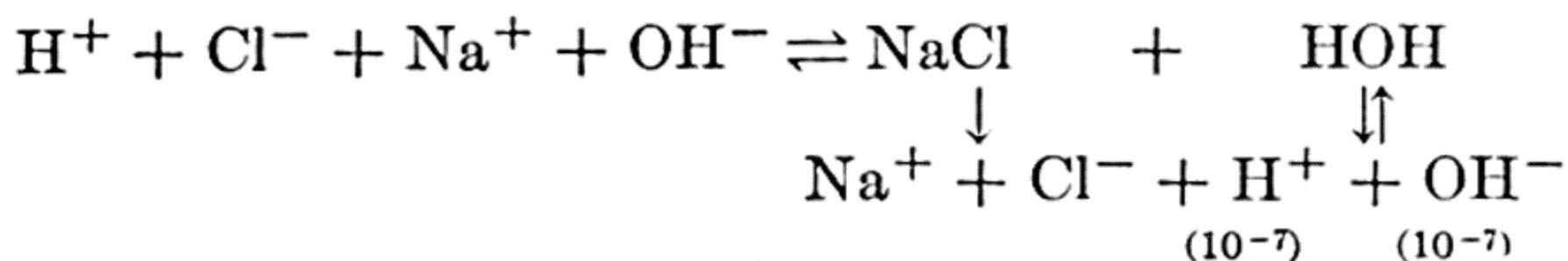


1 gram-mole of  $\text{NaCl}$  and 1 of  $\text{H}_2\text{O}$  are produced. The equation makes it appear that the reaction has gone absolutely to completion and, if it were possible to ignore the effect of the solvent, such would be the case. But we know that the water used as the solvent causes greater or less

ionization of all dissolved acids, bases and salts and results in a certain amount of hydrolysis. Then, since the neutralization is carried out in an aqueous solution, the first matter to decide is to what extent the reaction will be completed in aqueous solution.

If the HCl and NaOH solutions are mixed in such a way that the final volume is exactly 1 liter the completeness of the reaction is determined by the water equilibrium:  $C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$ . From this it is evident that there will remain in solution concentrations of hydrogen and hydroxyl ions such that their product is equal to  $1.2 \times 10^{-14}$ . Since the HCl, NaOH and the NaCl produced are all highly ionized and dissociate to about the same extent, there will be little or no tendency for the sodium ions to recombine with hydroxyl ions to form NaOH, nor for hydrogen ions to recombine with chloride ions to form HCl. The equilibrium concentrations, therefore, of  $H^+$  ions and  $OH^-$  ions remaining to satisfy the water constant are in equal amount. Their concentrations are  $1 \times 10^{-7}$  for  $H^+$  ion and  $1 \times 10^{-7}$  for  $OH^-$  ion, and the resulting solution is neutral. The equilibrium point comes at the exact neutrality point, and the reaction stops when there still remain in solution  $1 \times 10^{-7}$  gram-ion of hydrogen and  $1 \times 10^{-7}$  gram-ion of hydroxyl.

We have then, to sum up the conditions when equilibrium is established, for the neutralization of HCl by NaOH, the equilibrium equations



In general, the equilibrium point is reached for the interaction of a strongly ionized acid and a strongly ionized base at the strict neutrality point where the concentration of both ions is  $1 \times 10^{-7}$ . Hydrolysis is negligible with this pair.

**The Titration Curve of Strong Acid and Strong Base.** (a) IDEAL CASE. We will consider first an ideal case, the titration of 25 ml. of a 0.1 *N* solution of HCl by a 0.1 *N* solution of NaOH. At the outset, before any base is added, the normality of the solution is 0.1. Assuming complete ionization of this strong acid, the  $C_H$  is  $1 \times 10^{-1}$  and therefore the pH is 1.

The equivalent volume of 0.1 *N* NaOH is 25 ml. At the equivalence point strict neutrality will have been reached and the pH, as already shown, will be 7.

The course of the titration can be followed by calculating the pH values of the resulting solution as successive increments of the base are



added. Thus, when 5 ml. of the base have been added, there remain 20 ml. of unneutralized acid in a total volume of 30 ml. The normality, originally 0.1 *N*, will, however, have changed in the total volume of solution. The new normality is found from the inverse volume relationship

$$V_1N_1 = V_2N_2$$

$$20 \text{ ml.} \times 0.1 \text{ } N = 30 \text{ ml.} \times x \text{ } N$$

from which the normality is found to be 0.066. This corresponds to a  $C_{H^+}$  of  $6.6 \times 10^{-2}$  and a *pH* of 1.18.

In this manner, the *pH* values shown in Table IV have been calculated.

TABLE IV

THE NEUTRALIZATION OF A STRONG ACID BY A STRONG BASE

Ml. NaOH Added	Ml. HCl Remaining	Total Volume of Solution	Normality of Solution	$C_{H^+}$	<i>pH</i>
0	25.0	25.0	0.100	$1 \times 10^{-1}$	1.
5.0	20.0	30.0	0.066	$6.6 \times 10^{-2}$	1.18
12.5	12.5	37.5	0.033	$3.3 \times 10^{-2}$	1.48
20.	5.0	45.0	0.011	$1.1 \times 10^{-2}$	1.96
22.5	2.5	47.5	0.0053	$5.3 \times 10^{-3}$	2.28
24.0	1.0	49.0	0.0020	$2.0 \times 10^{-3}$	2.70
24.5	0.5	49.5	0.0010	$1.0 \times 10^{-3}$	3.00
24.9	0.1	49.9	0.0002	$2.0 \times 10^{-4}$	3.70
24.95	0.05	49.95	0.0001	$1.0 \times 10^{-4}$	4.00
25.0	0.0	50.0	0.0	$1.0 \times 10^{-7}$	7.00
25.05	-0.05	50.05	0.0001 (NaOH)	$1.2 \times 10^{-10}$	9.92
25.1	-0.1	50.1	0.0002 "	$6.0 \times 10^{-11}$	10.22
26.0	-1.0	51.0	0.002 "	$6.0 \times 10^{-12}$	11.22

Note that when one-half of the acid has been neutralized, in the resulting 37.5 ml. of solution, the *pH* is 1.48. When 25.95 ml. of base have been added and only a single drop of HCl remains, the *pH* is 4.00. At equivalence it is 7. Beyond this excess base is present, but a single drop, 0.05 ml., establishes the *pH* at 9.92, in the basic region.

In the graph in Fig. 7 such *pH* values have been plotted. The most significant thing about this curve is the wide range, from *pH* of 4 to *pH* of 10, over which the curve is practically coincident with the vertical axis representing the equivalent volume. A very small drop, about

0.05 ml., causes an enormous decrease in the hydrogen-ion concentration (a large increase in the  $pH$ ) in the vicinity of the neutrality point. This has an important bearing on the selection of suitable indicators for such a titration.

(b) PRACTICAL CASE. In a practical, rather than ideal, titration such as in the laboratory procedure for comparison of solutions, the two

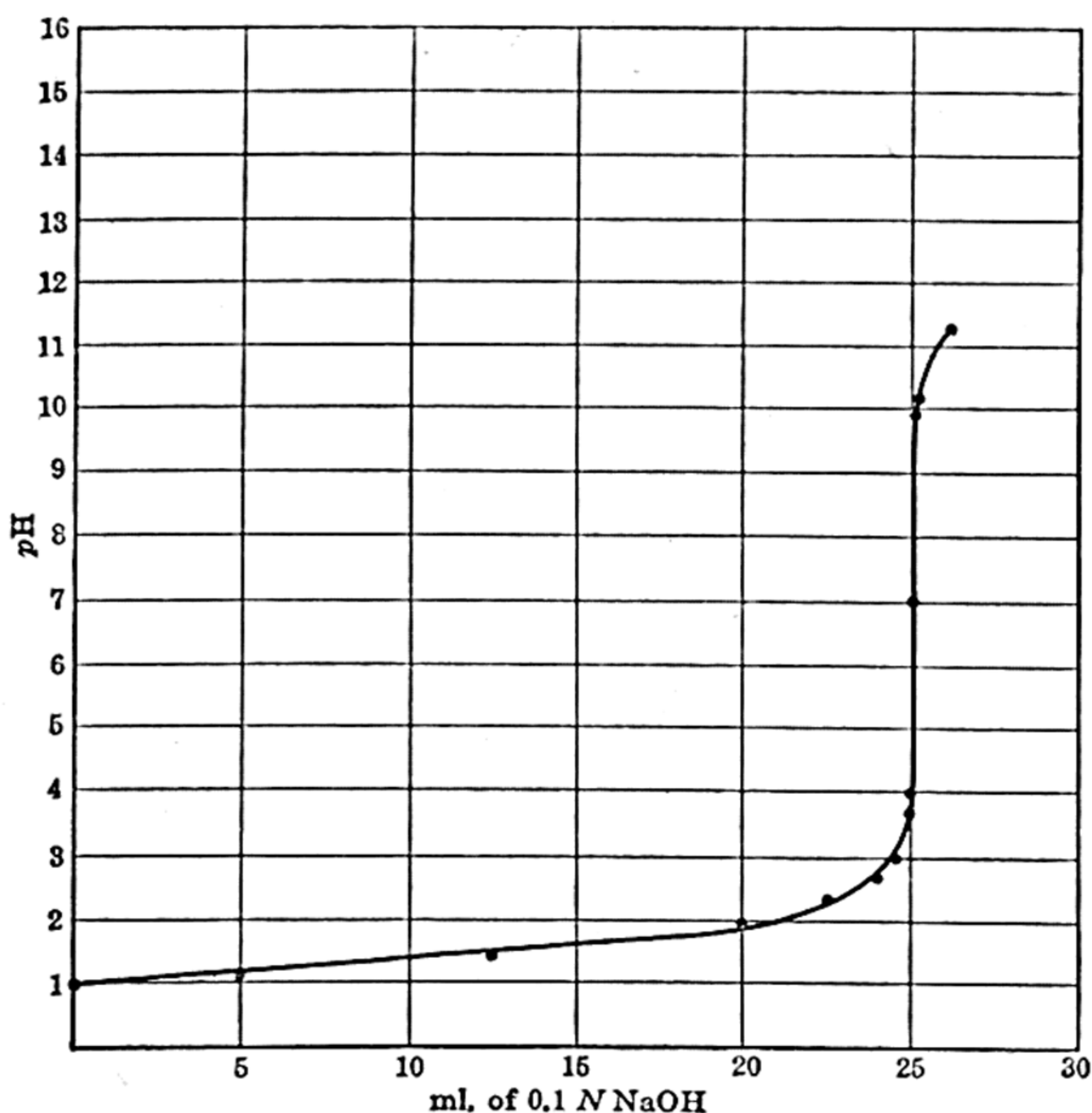


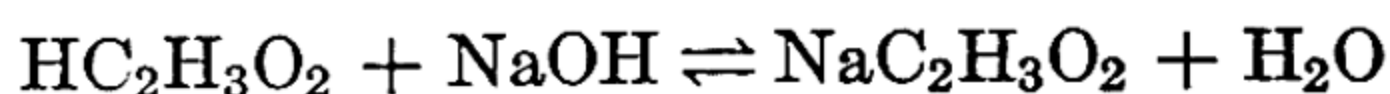
FIG. 7. Titration curve of 0.1 N HCl by 0.1 N NaOH.

solutions are rarely of the same strength and adjustment must therefore be made in the calculation of  $pH$  values used in the plotting of the graph. This somewhat complicates the computations. As an illustration, suppose that in making the comparison titration of acid against base it was found that 25 ml. of HCl required 30 ml. of NaOH and that, upon standardization, the HCl solution was shown to be 0.1234 N. At the point, for example, when 5 ml. of the acid will have been neutralized, the volume of base added is not 5 ml. as in the ideal case but  $30/25$  or  $1.20 \times 5 \text{ ml.} = 6.0 \text{ ml.}$  The total volume of solution is then 31.0 ml. of which 20.0 ml. are unneutralized acid of original normality 0.1234. The new normality is then found from the inverse volume relationship ( $V_1N_1 = V_2N_2$ ) and from this the  $C_{H^+}$  and finally the  $pH$  value can be found.



As a practical assignment, the student should calculate a series of  $pH$  values, for the titration of acid by base, on the basis of one of his comparison runs, using the normalities of acid and base as established by standardization. The  $pH$  values should then be plotted and the graph submitted.

**Reactions between Weak Acids and Strong Bases.** The extent to which the neutralization reaction for this pair takes place depends upon the extent to which the reverse reaction of hydrolysis takes place. Let us consider the neutralization of acetic acid,  $HC_2H_3O_2$ , by  $NaOH$ . When an exact equivalent of  $NaOH$  has been added to the  $HC_2H_3O_2$  present, the reaction would be complete if we ignored the water equilibrium and the hydrolysis effect. The neutralization of  $HC_2H_3O_2$  by  $NaOH$  according to the equation



leads to the formation of  $NaC_2H_3O_2$ , a salt which is highly ionized and which undergoes a certain amount of hydrolysis.

The hydrolysis is dependent in this case upon the feeble ionization of acetic acid. Since acetic acid is a weakly ionized electrolyte, hydrogen ions will be removed from the solution, leaving an excess of hydroxyl ions and resulting in a solution which is basic and not neutral. Equilibrium is therefore reached after the true neutrality point is passed, when base is added to acid.

**Titration Curve of Weak Acid and Strong Base.** (a) **IDEAL CASE.** The calculation of  $pH$  values, when, for example, 25 ml. of 0.1  $N$   $HC_2H_3O_2$  are titrated with 0.1  $N$   $NaOH$ , is complicated by the fact that the presence of  $NaC_2H_3O_2$  formed in the reaction acts by common-ion effect and, as previously shown, the equivalence point is displaced from neutrality because of hydrolysis.

The initial  $pH$  can be directly calculated from the normality of the solution and its degree of ionization:

$$C_{H^+} = 0.1 \times 0.0134 = 1.34 \times 10^{-3}$$

from which  $pH = 2.9$ .

Or, if the degree of ionization is not known,  $C_{H^+}$  can be obtained from the Ostwald dilution formula, substituting  $N$  for  $M$

$$\frac{M\alpha \times M\alpha}{M(1 - \alpha)} = K_{ion}$$

$$0.1 \alpha^2 = 1.8 \times 10^{-5} \quad (\text{neglecting the small amount of } HC_2H_3O_2 \text{ which ionizes})$$

Whence  $\alpha$ , the degree of ionization multiplied by  $M$  (or  $N$ , the normality), gives

$$C_{H^+} = 1.3 \times 10^{-3} \quad \text{and} \quad pH = 2.9$$

When an equivalent volume of base has been added (25.00 ml. of 0.1  $N$  NaOH), equilibrium will be reached. The  $pH$  of the solution at the equivalence point is calculated in the following manner. The hydrolysis is dependent upon the amount of  $NaC_2H_3O_2$  formed; it is therefore simpler to arrive at the value by considering the hydrolysis of a  $NaC_2H_3O_2$  solution. In an aqueous solution of  $NaC_2H_3O_2$  final equilibrium depends not only on satisfying the water equilibrium

$$C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$$

but also on the acetic acid equilibrium which is controlled by its ionization constant:

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = 1.8 \times 10^{-5}$$

The hydrolysis equilibrium is then jointly controlled by the two equilibria and if we divide the former by the latter

$$\frac{C_{H^+} \times C_{OH^-}}{C_{H^+} \times C_{C_2H_3O_2^-}} = \frac{K_w}{K_{ion}} = \frac{1.2 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$C_{HC_2H_3O_2}$$

we get the hydrolysis expression

$$\frac{C_{OH^-} \times C_{HC_2H_3O_2}}{C_{C_2H_3O_2^-}} = 6.7 \times 10^{-10}$$

where  $6.7 \times 10^{-10}$  is the hydrolysis constant for  $NaC_2H_3O_2$ ,  $C_{OH^-}$  is the hydroxyl-ion concentration at equilibrium,  $C_{HC_2H_3O_2}$  is the concentration of acetic acid formed in the hydrolysis and  $C_{C_2H_3O_2^-}$  is the concentration of the ion of the salt formed. The value of  $C_{OH^-}$  equals that of  $C_{HC_2H_3O_2}$  because for every ion of hydrogen combined to form  $HC_2H_3O_2$  a hydroxyl ion is left in excess.

If in a titration we add 25 ml. of 0.1  $N$  NaOH to 25 ml. of 0.1  $N$   $HC_2H_3O_2$  they will have reacted in equivalent proportions. The amount of  $NaC_2H_3O_2$  would be 0.1 normal, but since the volume of the mixture is now 50 ml. the concentration of the salt, and hence that of the  $C_2H_3O_2^-$  ion, is 0.05 normal (or molar). Letting  $x$  stand for the  $OH^-$  concen-



tration, as well as the acetic acid concentration formed by hydrolysis, we have

$$\frac{x \times x}{(0.05 - x)} = 6.7 \times 10^{-10}$$

As an approximation, since the amount of  $C_2H_3O_2^-$  ion combined is negligibly small, we can write

$$\frac{x^2}{0.05} = 6.7 \times 10^{-10}$$

$$x = 5.8 \times 10^{-6}$$

Since

$$C_{H^+} = \frac{K_w}{C_{OH^-}} \quad (\text{from the water equilibrium})$$

$$\begin{aligned} C_{H^+} &= \frac{1.2 \times 10^{-14}}{5.8 \times 10^{-6}} \\ &= 2.07 \times 10^{-9} \end{aligned}$$

corresponding to a pH of 8.68, or approximately 8.7.

The steps in this calculation can be shortened, for since

$$\frac{C_{OH^-} \times C_{HC_2H_3O_2}}{C_{C_2H_3O_2^-}} = \frac{K_w}{K_{ion}}$$

and  $C_{HC_2H_3O_2}$  is equal to  $C_{OH^-}$

$$(C_{OH^-})^2 = \frac{K_w \times C_{C_2H_3O_2^-}}{K_{ion}}$$

From the water equilibrium,

$$C_{OH^-} = \frac{K_w}{C_{H^+}}$$

and solving for  $C_{H^+}$ ,

$$C_{H^+} = \sqrt{\frac{K_w \times K_{ion}}{C_{C_2H_3O_2^-}}}$$

$$C_{H^+} = \sqrt{\frac{1.2 \times 10^{-14} \times 1.8 \times 10^{-5}}{0.05}} = 2.07 \times 10^{-9}$$

corresponding, as before, to a pH of 8.68.

When 5 ml. of 0.1 N NaOH are added the total volume is 30 ml., of which 20 ml. are unneutralized 0.1 N acetic acid. The new normality of the  $HC_2H_3O_2$  is, as in the case of HCl (see page 70), therefore 0.066.

The  $\text{C}_2\text{H}_3\text{O}_2^-$ -ion concentration corresponds to 5 ml. of 0.1  $N$   $\text{NaC}_2\text{H}_3\text{O}_2$  in 30 ml. or, from the inverse relation  $V_1N_1 = V_2N_2$ , the normality of the salt is 0.0167. Substituting these values in the equation

$$\begin{aligned} C_{\text{H}^+} &= \frac{C_{\text{HC}_2\text{H}_3\text{O}_2} \times K_{\text{ion}}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} \\ &= \frac{0.066}{0.0166} \times 1.8 \times 10^{-5} \\ &= 7.22 \times 10^{-5} \end{aligned}$$

It will be noted that the ratio 0.066/0.166, which represents the concentration of acetic acid and acetate ion, respectively, is the same as the

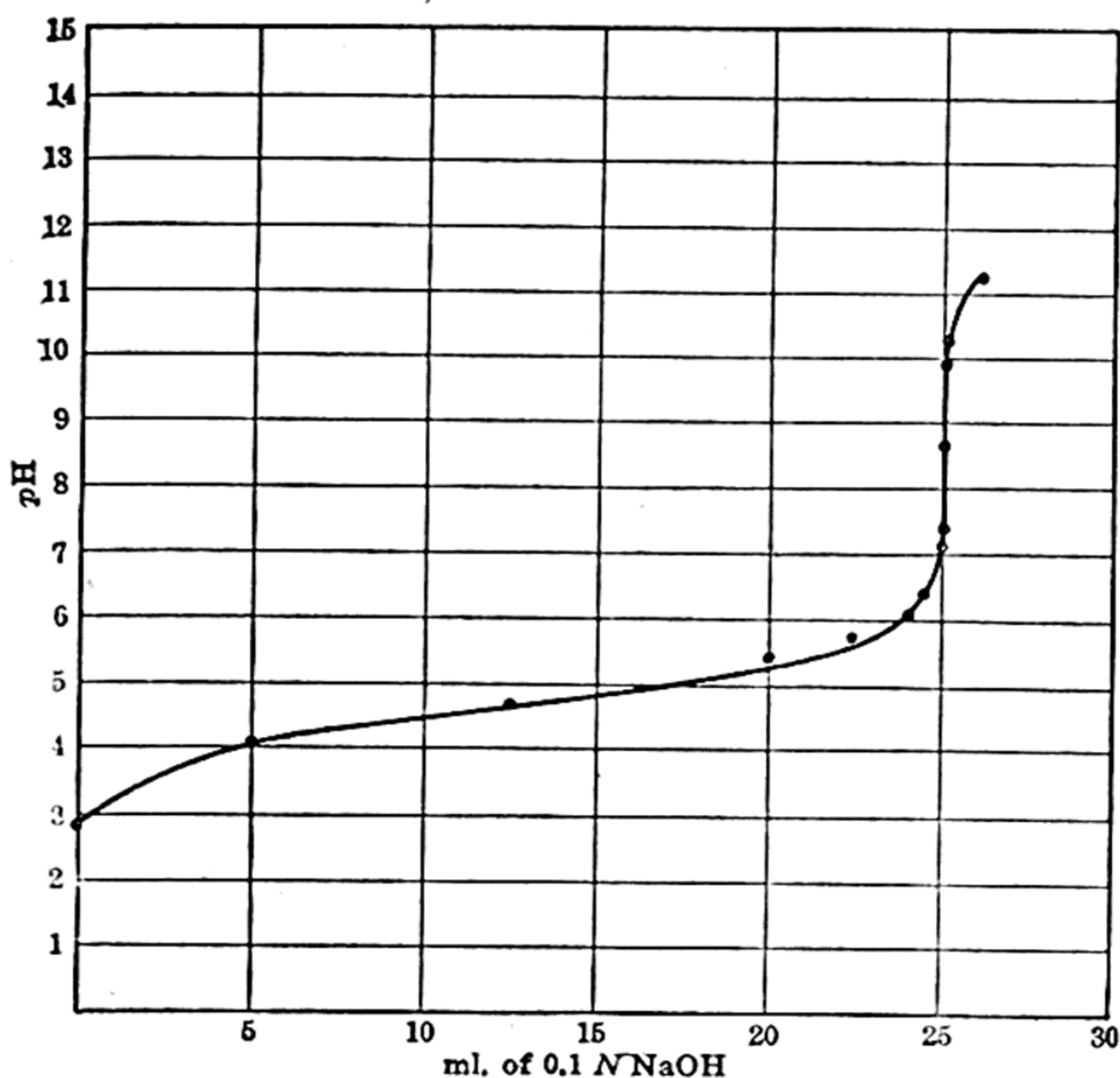


FIG. 8. Titration curve of 0.1  $N$   $\text{HC}_2\text{H}_3\text{O}_2$  by 0.1  $N$   $\text{NaOH}$ .

ratio of the volumes of 0.1  $N$  solutions, namely 20 ml. of acid and 5 ml. of  $\text{NaC}_2\text{H}_3\text{O}_2$ . That is

$$\frac{0.066}{0.0166} = \frac{20 \text{ ml.}}{5 \text{ ml.}}$$

This simplifies the calculation, so that here, as well as at all other desired pH values, we can substitute volumes for normalities directly.



For all points up to and including the addition of 24.95 ml. of 0.1 *N* NaOH, the following formula can be used:

$$C_{H^+} = \frac{\text{Volume of acid remaining}}{\text{Volume of NaOH added}} \times 1.8 \times 10^{-5}$$

Values of *pH* calculated in this way are tabulated in Table V and shown graphically in Fig. 8.

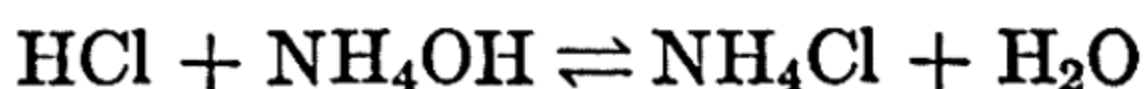
TABLE V

NEUTRALIZATION OF A WEAK ACID BY A STRONG BASE

Ml. NaOH Added	Ml. HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> Remaining	Total Volume of Solution	<i>C</i> <sub>H<sup>+</sup></sub>	<i>pH</i>
0	25.0	25.0	$1.3 \times 10^{-3}$	2.9
5.0	20.0	30.0	$7.2 \times 10^{-5}$	4.1
12.5	12.5	37.5	$1.8 \times 10^{-5}$	4.7
20.0	5.0	45.0	$4.5 \times 10^{-6}$	5.4
22.5	2.5	47.5	$2.0 \times 10^{-6}$	5.7
24.0	1.0	49.0	$7.5 \times 10^{-7}$	6.1
24.5	0.5	49.5	$3.7 \times 10^{-7}$	6.4
24.9	0.1	49.9	$7.4 \times 10^{-8}$	7.1
24.95	0.05	49.95	$8.6 \times 10^{-8}$	7.4
25.0	0.0	50.0	$2.07 \times 10^{-9}$	8.7
25.05	-0.05	50.05	$1.2 \times 10^{-10}$	9.9
25.1	-0.1	50.1	$6.0 \times 10^{-11}$	10.2
26.0	-1.0	51.0	$6.0 \times 10^{-12}$	11.2

(b) PRACTICAL CASE. As an assignment it is suggested that the student either prepare a small amount of approximately 0.1 *N* acetic acid, titrating 25 ml. of it with standard NaOH or else that similar data be furnished him, from which he can calculate a series of *pH* values and construct the graph.

**Reactions between Strong Acids and Weak Bases.** A third type of neutralization reaction is that between a strong acid and a weak base, such as, for example, that between HCl and NH<sub>4</sub>OH. Here the salt formed is NH<sub>4</sub>Cl, according to the equation



The extent to which the ions of this salt will react with the ions of water depends upon the degree of ionization of NH<sub>4</sub>OH, the weakly ionized base concerned in the equilibrium. Since some hydroxyl ions are used

up in the formation of the salt of the weak base, an excess of hydrogen ions remains, giving a solution which at equilibrium is acidic. In fact, a calculation from the hydrolysis constant will show equilibrium to be reached for a 0.1 *N* solution of ammonium chloride at a *pH* value of about 5.24.

**Titration Curve of Strong Acid and Weak Base.** The titration of a strong acid by a standard weak base is never carried out in practice, but the reverse, the titration of weak bases, such as  $\text{NH}_4\text{OH}$  by standard  $\text{HCl}$ , is of frequent occurrence. The course of the reaction is analogous to that just considered for  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaOH}$ , but the *pH* values are reversed. Let us consider the titration of 25 ml. of 0.1 *N*  $\text{NH}_4\text{OH}$  with 0.1 *N*  $\text{HCl}$ .

The *pH* of the original solution may be found either from the degree of ionization or from the ionization constant. In the first method, the solution being 0.1 *N* and the degree of ionization being 1.31 per cent, the  $C_{\text{OH}^-}$  is  $0.1 \times 0.0131 = 0.00131$  or  $1.31 \times 10^{-3}$ . Therefore

$$C_{\text{H}^+} = \frac{1.2 \times 10^{-14}}{1.31 \times 10^{-3}} = 1 \times 10^{-11.04}$$

and

$$p\text{H} = 11.04$$

In the latter case, using the equilibrium

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = K_{\text{ion}}$$

$$C_{\text{OH}^-} = \sqrt{K_{\text{ion}} \times C_{\text{NH}_4\text{OH}}} = 1.32 \times 10^{-3}$$

Therefore,

$$C_{\text{H}^+} = \frac{K_{\text{w}}}{C_{\text{OH}^-}} \quad \text{and} \quad p\text{H} = \log \frac{1}{C_{\text{H}^+}}$$

$$p\text{H} = 11.04$$

For values of *pH*, up to the addition of about 24.95 ml. of 0.1 *N*  $\text{HCl}$ , the normality of the remaining base and the normality of the  $\text{NH}_4\text{Cl}$  formed may be evaluated or, alternatively, as in the case of acetic acid, the ratio of volumes may be taken. By combining

$$K_{\text{w}} = C_{\text{H}^+} \times C_{\text{OH}^-} \quad \text{and} \quad K_{\text{ion}} = \frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}}$$

we have

$$C_{\text{H}^+} = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_4\text{OH}}} \times \frac{K_{\text{w}}}{K_{\text{ion}}}$$



For example, when 5 ml. of acid have been added there remain 20 ml. of unneutralized  $\text{NH}_4\text{OH}$  and there were formed 5 ml. of  $\text{NH}_4\text{Cl}$ .

$$\begin{aligned} C_{\text{H}^+} &= \frac{5}{20} \times \frac{1.2 \times 10^{-14}}{1.75 \times 10^{-5}} \\ &= 1.7 \times 10^{-10} \end{aligned}$$

Therefore

$$\text{pH} = 9.77$$

Calculation of other points is left for the student.

Points beyond the equivalent volume, when an excess of acid is present, have the same pH values as already calculated, on page 70, for the  $\text{HCl-NaOH}$  titration.

The pH value attained at equivalence is calculated, from the hydrolysis formula, in a manner analogous to that for  $\text{NaC}_2\text{H}_3\text{O}_2$ . Here the water equilibrium and the ionization constant of  $\text{NH}_4\text{OH}$  are the controlling factors.

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4^+} \times C_{\text{OH}^-}} = \frac{K_w}{K_{\text{ion}}}$$

Whence

$$\frac{C_{\text{H}^+} \times C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+}} = \frac{1.2 \times 10^{-14}}{1.75 \times 10^{-5}} = 6.9 \times 10^{-10}$$

As before, if 25 ml. of 0.1  $N$   $\text{HCl}$  react with 25 ml. of 0.1  $N$   $\text{NH}_4\text{OH}$ , we have at equivalence a 0.05  $N$  solution of  $\text{NH}_4\text{Cl}$ . Letting  $x$  equal  $C_{\text{H}^+}$  as well as  $C_{\text{NH}_4\text{OH}}$ ,

$$\frac{x \times x}{0.05} = 6.9 \times 10^{-10}$$

$$C_{\text{H}^+} = 5.9 \times 10^{-6}$$

Instead of using the value of the hydrolysis constant, equations can be combined to read

$$C_{\text{H}^+} = \sqrt{\frac{K_w \times C_{\text{NH}_4^+}}{K_{\text{ion}}}}$$

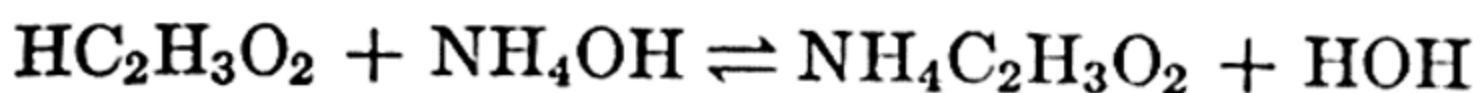
and we have

$$\begin{aligned} C_{\text{H}^+} &= \sqrt{\frac{1.2 \times 10^{-14} \times 5 \times 10^{-2}}{1.75 \times 10^{-5}}} \\ &= 5.9 \times 10^{-6} \end{aligned}$$

This corresponds to a pH of 5.24.

The graph in Fig. 9 shows the course of the neutralization of  $\text{NH}_4\text{OH}$  by  $\text{HCl}$ .

**Reactions between Weak Acids and Weak Bases.** The fourth case may be illustrated by the following reaction:



in which the hydrolysis reaction, that is, the reaction from right to left, is to be considered. In this case  $\text{OH}^-$  ions react with  $\text{NH}_4^+$  ions from

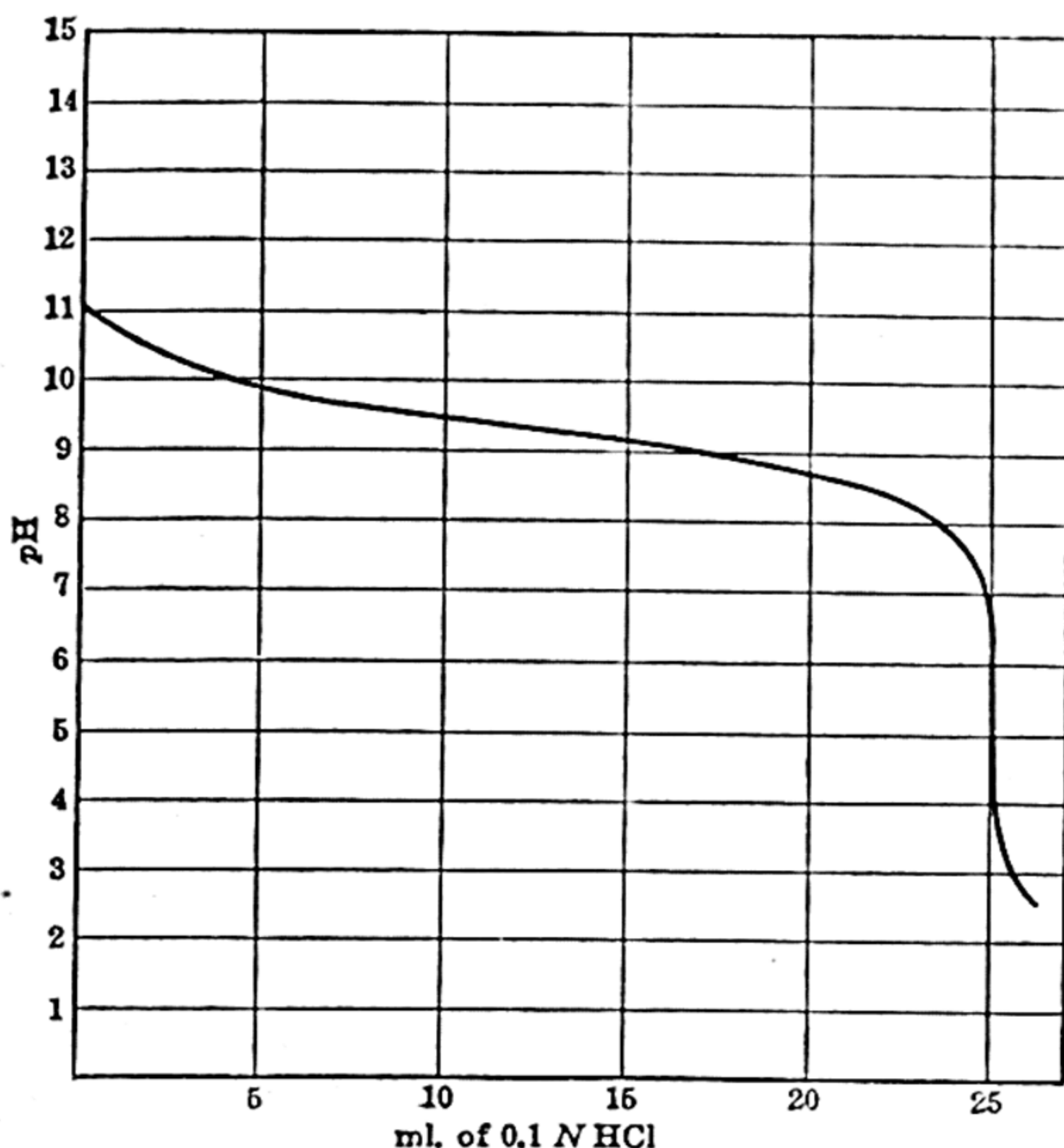


FIG. 9. Titration curve of 0.1 N  $\text{NH}_4\text{OH}$  by 0.1 N  $\text{HCl}$ .

the  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  to form the weakly ionized base and, at the same time,  $\text{H}^+$  ions react with  $\text{C}_2\text{H}_3\text{O}_2^-$  ions to produce the weakly ionized acid. For final equilibrium the ionization constants for both  $\text{NH}_4\text{OH}$  and  $\text{HC}_2\text{H}_3\text{O}_2$  must be satisfied as well as the relation

$$C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$$

Since both acid and base are weakly ionized, hydrogen ions as well as hydroxyl ions are removed to form the acid and base. In this particular case it happens that  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NH}_4\text{OH}$  are ionized to almost exactly the same extent. Consequently almost the same quantities of hydrogen



and hydroxyl ions are removed, resulting in a solution which is almost exactly neutral.

The course of the reaction presents some interesting characteristics but, in practice, such a titration is not made, because no indicator can be employed for the titration, nor can the end point be found in a potentiometric titration.

If we take, for example, the reaction between 0.1 *N* HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and 0.1 *N* NH<sub>4</sub>OH the following characteristics are to be observed.

1. If the acid is being neutralized by the addition of base, the initial *pH* of the solution, as already computed on page 73, will be 2.9, and, conversely, if base is being neutralized by acid, the initial *pH* of a 0.1 *N* NH<sub>4</sub>OH solution is 11.04.

2. *pH* values for points up to practically the equivalent point are identical with those already calculated or discussed for either the acetic acid or the ammonium hydroxide titrations as the case may be.

3. The equivalence point, since both acid and base are about equally ionized, will have a *pH* of practically 7. In cases where both reactants are weakly ionized, but one is somewhat stronger than the other, the  $C_{H^+}$  can be calculated from the formula derived below.

The ionization equilibrium for the weak acid is

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K_{acid}$$

and for the base

$$\frac{C_{OH^-} \times C_{NH_4^+}}{C_{NH_4OH}} = K_{base}$$

and for water

$$C_{H^+} \times C_{OH^-} = K_w$$

Therefore

$$\frac{C_{H^+} \times C_{OH^-}}{\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} \times \frac{C_{OH^-} \times C_{NH_4^+}}{C_{NH_4OH}}} = \frac{K_w}{K_{acid} \times K_{base}}$$

The expression just given is the hydrolysis equilibrium for NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. In its simpler form it is

$$\frac{C_{HC_2H_3O_2} \times C_{NH_4OH}}{C_{C_2H_3O_2^-} \times C_{NH_4^+}} = \frac{K_w}{K_{acid} \times K_{base}} = K_{hyd} \quad (1)$$

Since the salt is a strong electrolyte

$$C_{NH_4^+} = C_{C_2H_3O_2^-}$$

and assuming practically equal concentrations of acid and base formed in hydrolysis

$$C_{\text{NH}_4\text{OH}} = C_{\text{HC}_2\text{H}_3\text{O}_2}$$

From equation 1 therefore

$$\frac{C_{\text{HC}_2\text{H}_3\text{O}_2}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = \frac{C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+}}$$

and therefore

$$\frac{(C_{\text{HC}_2\text{H}_3\text{O}_2})^2}{(C_{\text{C}_2\text{H}_3\text{O}_2^-})^2} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}}$$

or

$$C_{\text{HC}_2\text{H}_3\text{O}_2} = C_{\text{C}_2\text{H}_3\text{O}_2^-} \sqrt{\frac{K_w}{K_{\text{acid}} \times K_{\text{base}}}}$$

The hydrolysis equation for the salt of a weak acid as given on page 74 is

$$\frac{C_{\text{HC}_2\text{H}_3\text{O}_2} \times C_{\text{OH}^-}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = \frac{K_w}{K_{\text{acid}}}$$

from which

$$C_{\text{HC}_2\text{H}_3\text{O}_2} = \frac{K_w \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{K_{\text{acid}} \times C_{\text{OH}^-}} \quad (2)$$

Equating 1 and 2 since both equal  $C_{\text{HC}_2\text{H}_3\text{O}_2}$ ,

$$\frac{K_w \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{K_{\text{acid}} \times C_{\text{OH}^-}} = C_{\text{C}_2\text{H}_3\text{O}_2^-} \sqrt{\frac{K_w}{K_{\text{acid}} \times K_{\text{base}}}}$$

$$\frac{(K_w)^2}{(K_{\text{acid}})^2 \times (C_{\text{OH}^-})^2} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}}$$

Solving for  $C_{\text{OH}^-}$

$$C_{\text{OH}^-} = \sqrt{\frac{K_w \times K_{\text{base}}}{K_{\text{acid}}}}$$

acid since  $C_{\text{OH}^-} = \frac{K_w}{C_{\text{H}^+}}$  therefore

$$C_{\text{H}^+} = \sqrt{\frac{K_w \times K_{\text{acid}}}{K_{\text{base}}}}$$

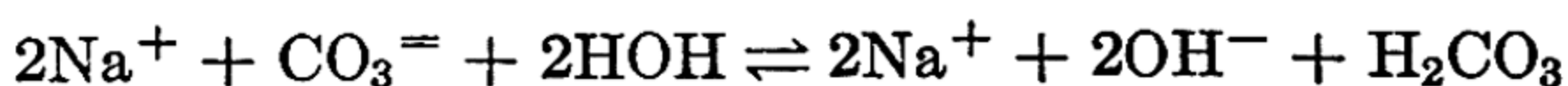
From this equation the hydrogen-ion concentration and the pH value at equivalence can be calculated, provided that the ionization constants



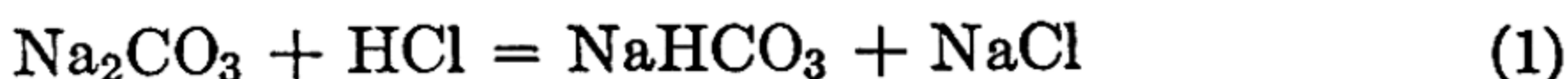
for the acid and base do not differ too much. In the case of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , the acid and base constants are substantially  $1.8 \times 10^{-5}$ , from which it follows that the pH at equivalence is practically 7.

**Titration of Sodium Carbonate Solutions.** If a salt of a strong base and a weak acid or a salt of a weak base and a strong acid is present in a solution, it is possible to titrate such a solution with a standard acid or base. Examples of such salts are sodium carbonate, borax and aluminum sulfate. The case of sodium carbonate is important since this salt is used for the standardization of HCl and enters largely in determinations of alkalinity.

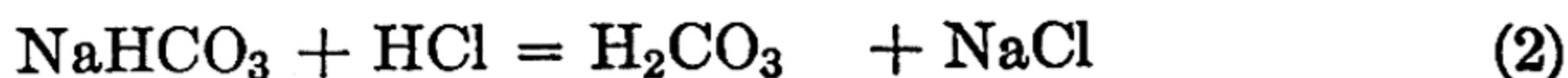
Sodium carbonate is the salt of the strong base, NaOH, and the weak acid,  $\text{H}_2\text{CO}_3$ . It will therefore hydrolyze to a considerable extent, giving a solution which is basic:



due to the repression of  $\text{H}^+$  ions in forming the slightly ionized carbonic acid. When acid such as HCl is added, the free  $\text{OH}^-$  ions are neutralized. When one equivalent of HCl is added, the bicarbonate is formed; when two equivalents are added the reaction is practically complete:



and



There are two equilibrium constants which must be satisfied, namely,  $C_{\text{H}^+} \times C_{\text{OH}^-} = K_w$  and the ionization constant for  $\text{H}_2\text{CO}_3$ :

$$\frac{(C_{\text{H}^+})^2 \times C_{\text{CO}_3^{2-}}}{C_{\text{H}_2\text{CO}_3}} = K_{\text{ion}}$$

The weakly ionized acid,  $\text{H}_2\text{CO}_3$ , is also unstable and readily decomposes into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , most of the  $\text{CO}_2$  escaping as a gas and only enough remaining to maintain the equilibrium

$$\frac{C_{\text{CO}_2} \times C_{\text{H}_2\text{O}}}{C_{\text{H}_2\text{CO}_3}} = K_{\text{H}_2\text{CO}_3}$$

By carrying out the titration in a hot solution the amount of  $\text{CO}_2$ , and therefore  $\text{H}_2\text{CO}_3$ , remaining is reduced to an extremely small amount.

In a cold solution the titration curve of sodium carbonate shows two vertical portions, corresponding to two equilibrium points, the first when one equivalent of acid is added, showing the formation of the bicar-

bonate, and the second, a better-defined and sharper portion of the curve, coming when two equivalents of standard acid are added and showing the complete neutralization of the carbonate. This second point occurs in the region sensitive to methyl orange indicator.

## INDICATOR THEORY

An indicator is a substance which must give a sudden color change in the region of the equilibrium point. That is, it must change its color at a  $pH$  value which is as near as possible to the equilibrium point reached in the neutralization. With the facts of hydrolysis in mind and having considered the electrometric method by which this point can be experimentally determined for typical pairs of acids and bases, the selection of the proper indicator now becomes a simple matter.

TABLE VI

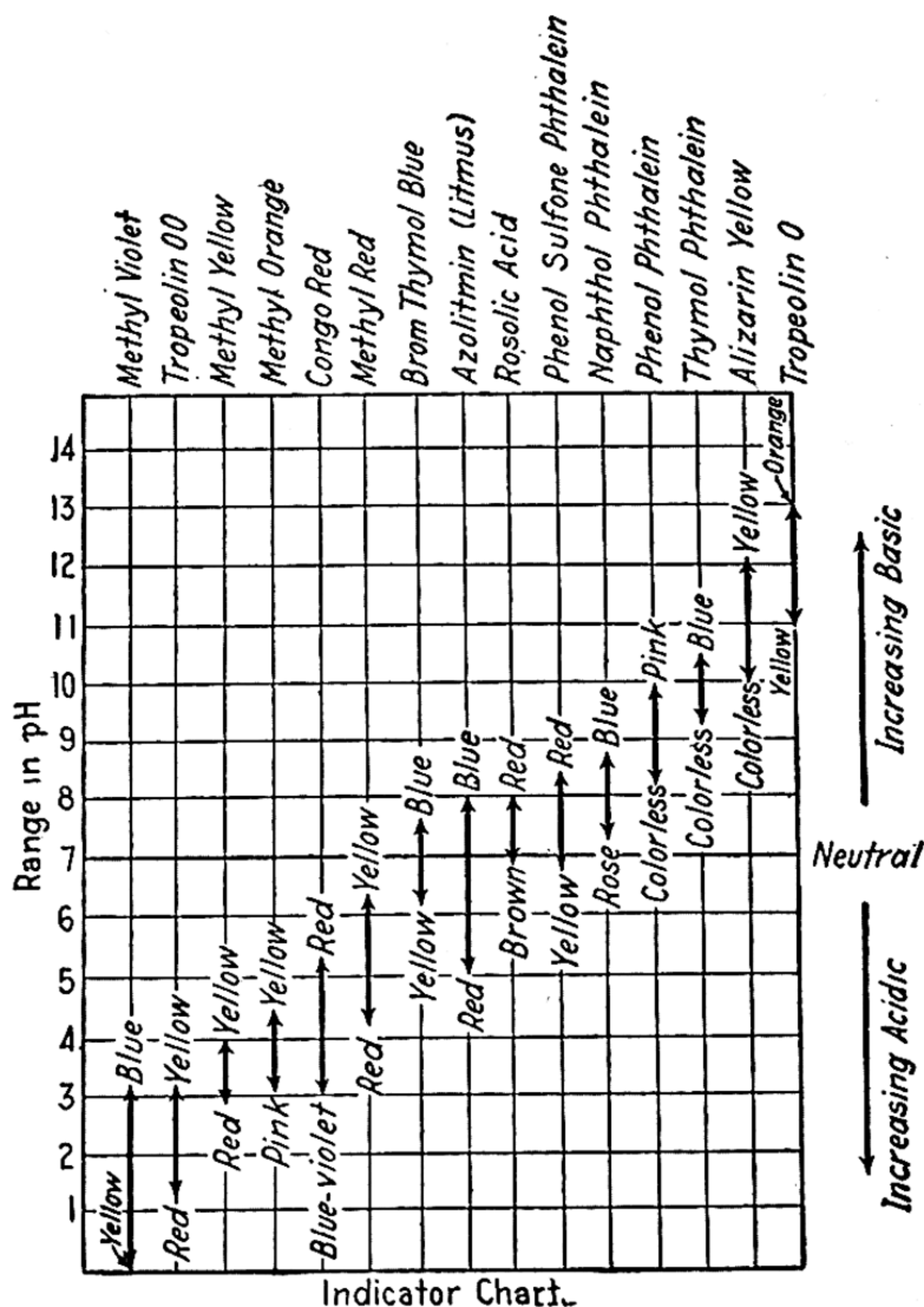
INDICATOR LIST

Indicator	Transition Range in $pH$	Color in Acid      →      Color in Base
Methyl violet	0.1– 3.2	Yellow → Green → Blue
Tropeolin OO	1.3– 3.2	Red → Yellow
Methyl yellow	2.9– 4.0	Red → Yellow
Methyl orange	3.1– 4.4	Pink → Yellow
Congo red	3.0– 5.2	Blue-violet → Red
Methyl red	4.2– 6.3	Red → Yellow
Brom-thymol blue	6.7– 7.6	Yellow → Blue
Azolitmin (litmus)	5.0– 8.0	Red → Blue
Rosolic acid	6.9– 8.0	Brown → Red
Phenol sulfonephthalein	6.8– 8.4	Yellow → Red
Naphtholphthalein	7.3– 8.7	Rose → Blue
Phenolphthalein	8.2–10.0	Colorless → Pink
Thymolphthalein	9.3–10.5	Colorless → Blue
Alizarine yellow	10.0–12.0	Yellow → Lilac
Tropeolin O	11.0–13.0	Yellow → Orange

A large number of organic compounds, chiefly dyestuffs and similar substances, have been found to show a marked color change over small ranges of hydrogen-ion concentration. These are the substances used as indicators. Table VI gives a selected list of indicators, showing the range in  $pH$  values over which the indicator changes color.



The color ranges of these indicators have been plotted in the accompanying chart. This is a handy arrangement for comparing pH ranges over which the indicator is sensitive with the pH ranges over which the equilibrium points occur as obtained from titration curves.



The neutralization curve for the neutralization of a strong acid by a strong base shows a rapid change in pH from about 4 to 9, as shown in Fig. 7, the equivalent point being theoretically at the neutrality point ( $pH = 7$ ). From the indicator chart it appears that brom-thymol blue, azolitmin, rosolic acid or phenol sulfonephthalein, which change color near the neutrality point, are ideal indicators to use. However, since the rate at which the hydrogen-ion concentration is changing is rapid in the regions just below and above the neutrality point, an indicator sensitive in either of those regions may be employed with little error. Thus methyl orange, which changes color at about  $pH = 4$ , if used will

give an end point slightly before the neutrality point is reached; and phenolphthalein, which changes color at about  $pH = 9$ , will give an end point after the neutrality point is passed. If 0.1 *N* solutions of the acid and base are used and 25 ml. of the acid are being titrated by the base, the end point for methyl orange occurs when 24.9 ml. of the alkali are added; and with phenolphthalein as indicator the end point comes at 25.1 ml. of added base. For this pair, therefore, either of these indicators may be used.

For the combination of weak acid and strong base, for which the equilibrium point lies in the region of excess hydroxyl-ion concentration, the titration curve has its vertical portion in the range of  $pH$  most sensitive to such indicators as phenolphthalein and naphtholphthalein. Phenolphthalein is the indicator commonly used here.

For the combination of strong acid and weak base, the equilibrium point is coincident with the range over which methyl orange is sensitive, that is, in a solution with high hydrogen-ion and correspondingly low hydroxyl-ion concentration. Methyl orange is the indicator commonly used for this pair.

Finally, a titration curve for the neutralization of a weak acid by a weak base will show no abrupt change, the changes in  $pH$  being gradual throughout the entire range. There is no indicator suited for this pair, and such a titration is impossible. Neutralization is, of course, possible, but there is no way of determining when equivalent amounts of the standard solution have been added to the unknown. If attempted as an experiment it will be found that with either of the two common indicators a gradual, shifting color change takes place which is of no value in finding the end point.

To sum up the conditions, the tabulation below will be useful.

Combination	Nature of Hydrolysis	Region of Equilibrium Point	Indicator
Strong acid + strong base	None (neutral)	$pH = 4-9$	M.O. or P.P.
Weak acid + strong base	Somewhat (basic)	$pH = 7-9$	P.P.
Strong acid + weak base	Somewhat (acidic)	$pH = 4-6$	M.O.
Weak acid + weak base	Somewhat (neutral)	None	None

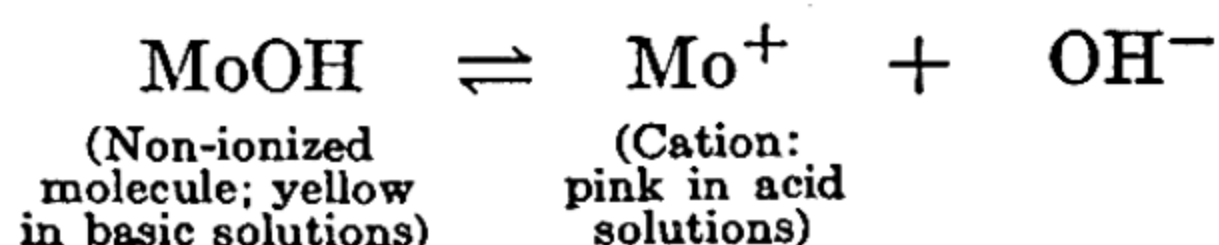
Several theories have been put forward to explain the cause of the color change of indicators. Two of these will be considered here. They are the ionization theory and the chromophoric theory.



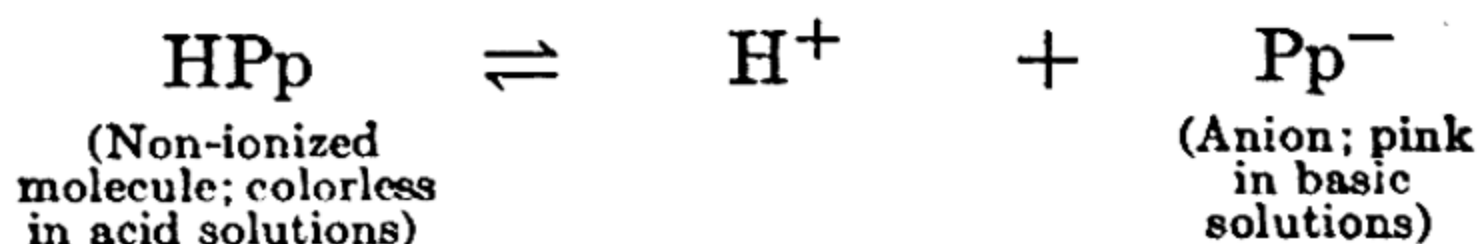
**Ionization Theory of Indicators.** According to this theory, first advanced by Ostwald, the substances used as indicators behave either as very weak acids or as very weak bases. That is, they ionize to a slight degree, and the color observed in a solution containing excess hydrogen or hydroxyl is due either to the color of the non-ionized molecule or to the color of the cation or anion of the indicator.

In the case of methyl orange, this indicator is a very weak base and can be considered as ionizing into  $\text{OH}^-$  ions and a cation which may be designated by the symbol  $\text{Mo}^+$ .

In water or in a basic solution the concentration of the cation  $\text{Mo}^+$  is extremely slight, and the yellow color of the solution is due to the non-ionized molecule. On the addition of an acid, a salt will be formed between the cations of the indicator and the anions of the acid, and this salt, ionizing, will increase the concentration of the cations  $\text{Mo}^+$ , which are pink in color. We have then:

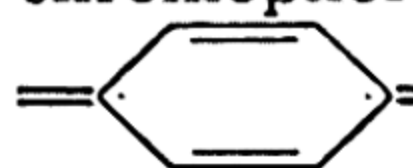


In the case of phenolphthalein, the indicator behaves as a very weakly ionized acid, ionizing into  $\text{H}^+$  ions and an anion which may be designated as  $\text{Pp}^-$ . This indicator is colorless in neutral and acidic solutions and pink in basic solutions. If a base is added, salt formation takes place between the cation of the base and the  $\text{Pp}^-$  anion, and this, by ionizing, increases the concentration of the anion and causes the solution to turn pink. The ionization of phenolphthalein can be shown thus:



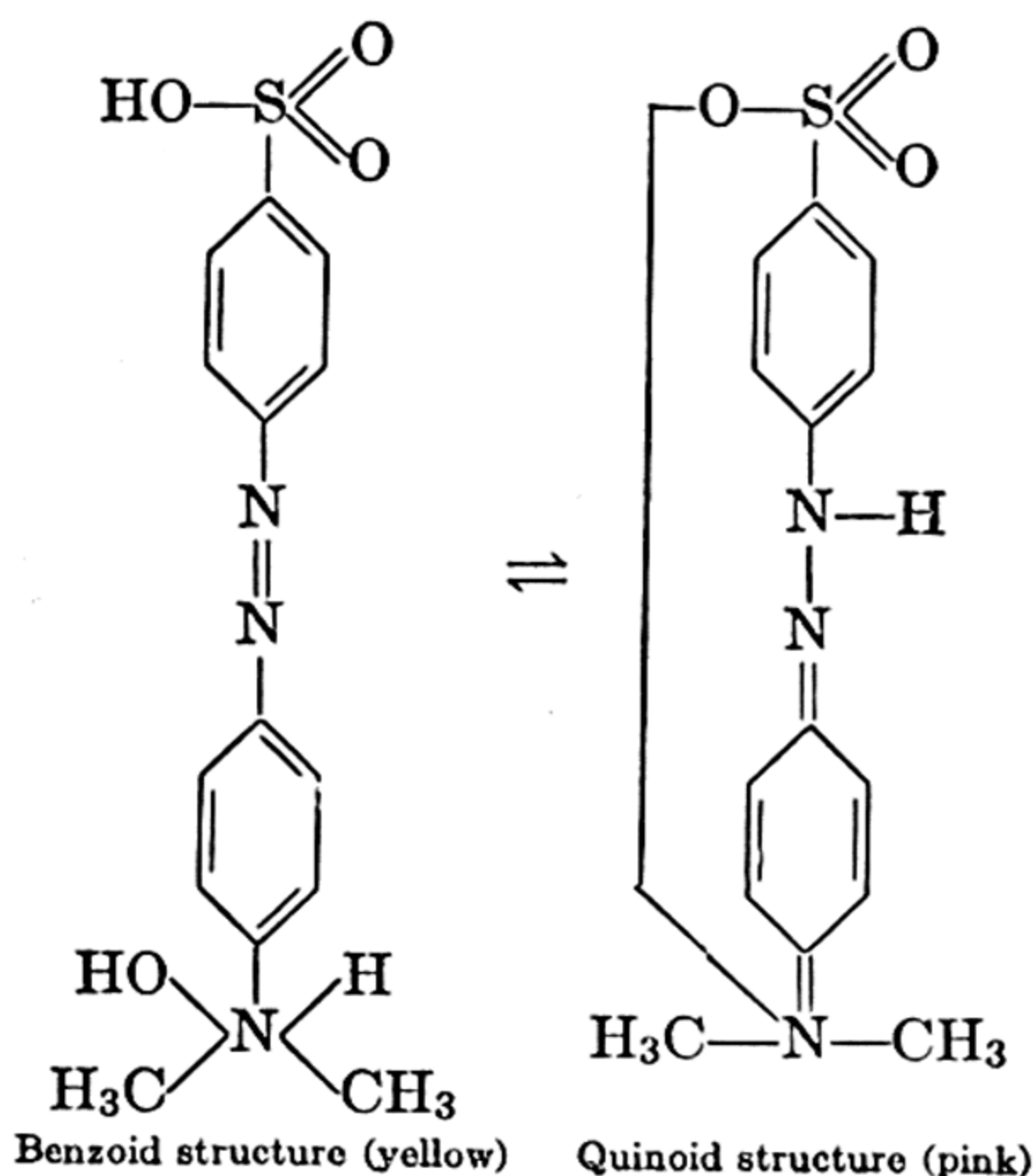
That this theory does not suffice to explain all the facts will be apparent when the chromophoric theory is presented.

**Chromophoric Theory of Indicators.** Investigation into the structure of organic dyestuffs, of which these indicators are representatives, has shown that the production of color or change of color is due to the presence of certain groups or radicals within the molecule, called chromophores, which possess a distinctive color. The quinoid group,

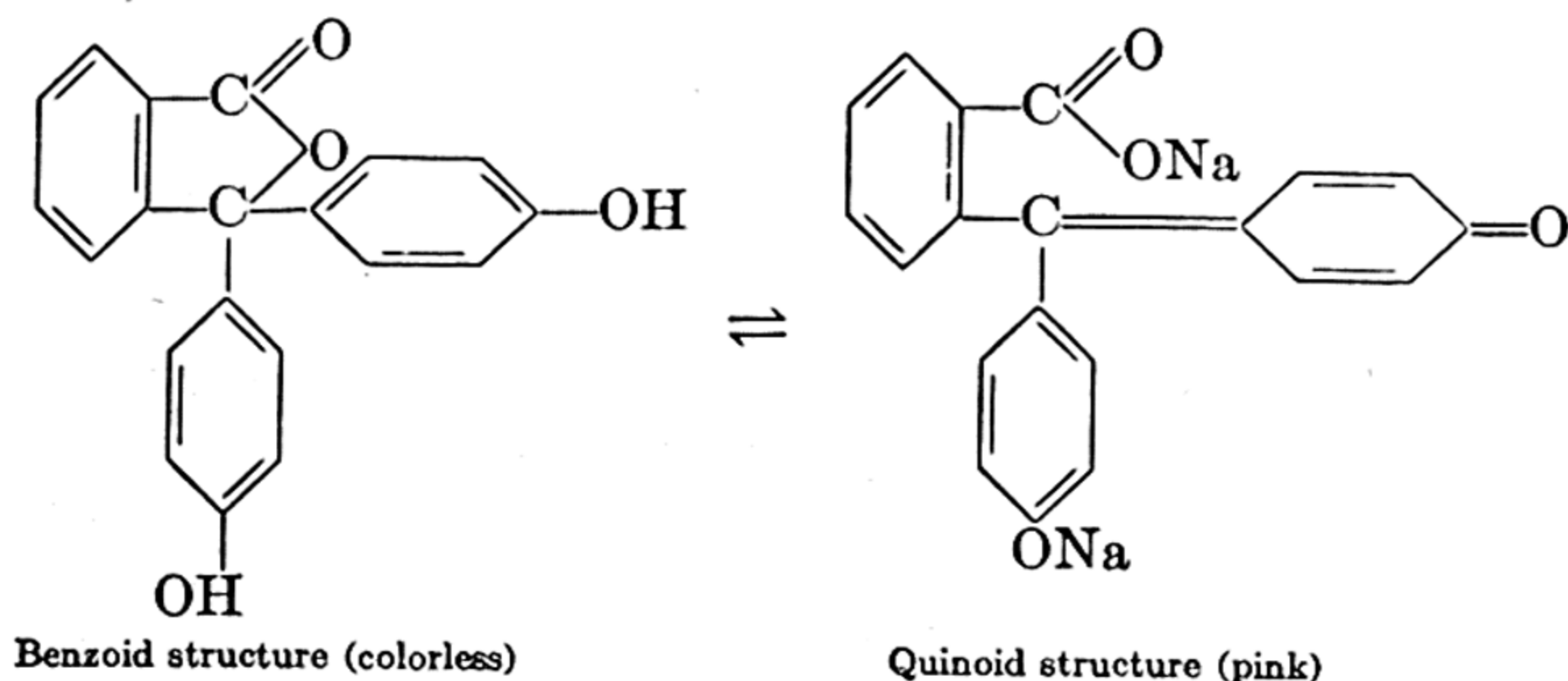


, is such a chromophoric group. A change of color is therefore due to an internal rearrangement of the atoms of the molecule, and tautomeric forms exist, one in basic solution, the other in acid solution.

For methyl orange, the two structures are:



For phenolphthalein, the tautomeric forms are:



In short, on the basis of this explanation, the change in structure takes place, in the case of methyl orange, at a  $pH$  value of about 4, and for phenolphthalein at a  $pH$  of about 8.

Methyl orange is thus most sensitive at low concentrations of  $OH^-$  ion and is commonly used for the titration of weak bases such as  $NH_4OH$ . Phenolphthalein, on the other hand, is sensitive to low  $H^+$ -ion concentrations and is used for the titration of weak acids such as  $HC_2H_3O_2$ .

## POTENTIOMETRIC TITRATION

Reference has already been made to a mode of titration in which the end point is indicated by a rapid change in the potential of the system,



rather than by the use of a chemical indicator. Such methods can be applied to acid-base titrations as well as to oxidation-reduction and to precipitation reactions. The potentiometric method for neutralization reactions is here briefly described.

A potentiometric acid-base titration consists, in brief, of making a series of  $pH$  determinations as standard base is being added to the acid or vice versa. As the equivalent volume is being approached there will be progressive rapid change in the  $pH$  value, and on passing through the equivalence point the change in  $pH$  will be most rapid.

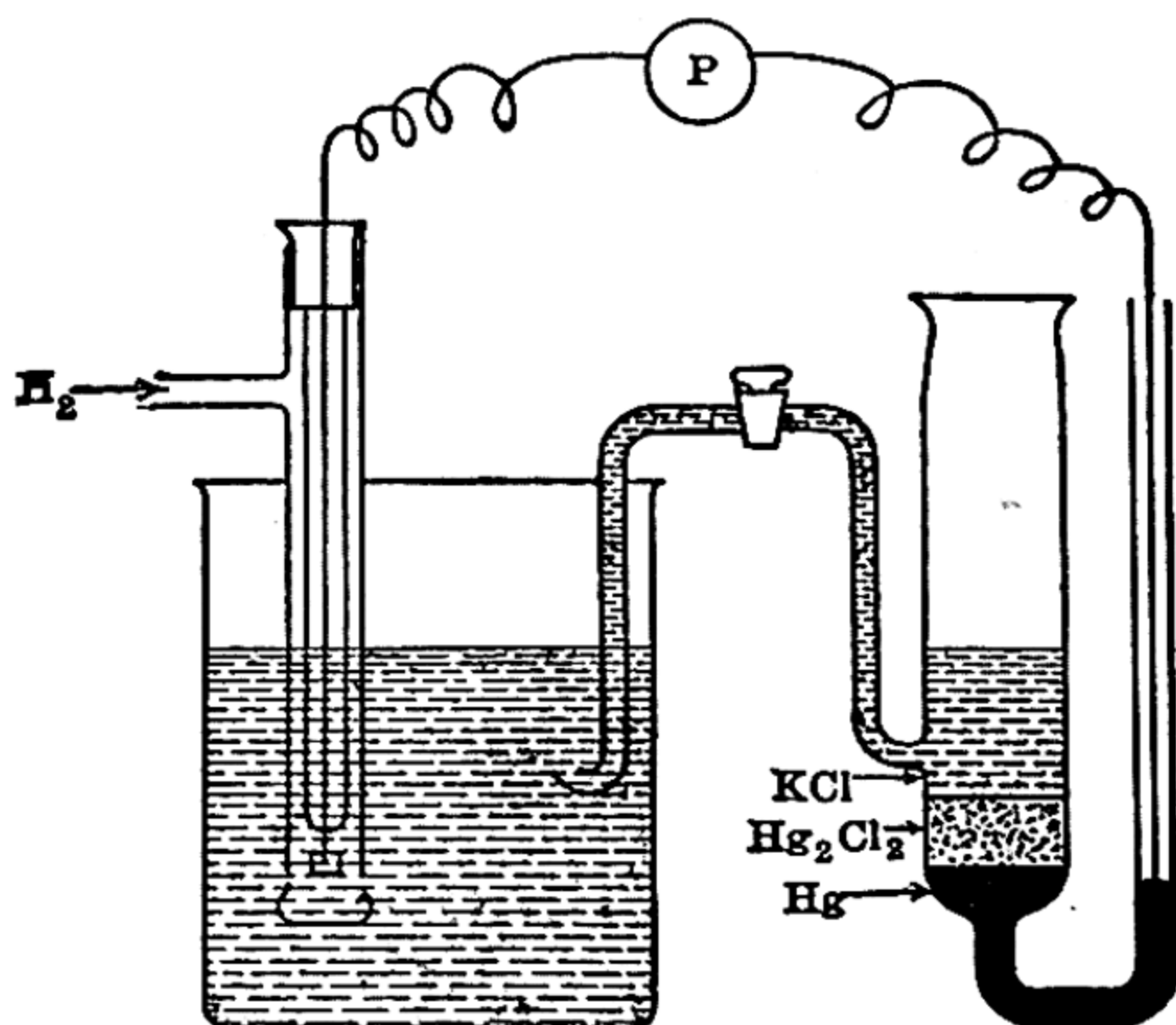


FIG. 10. Potentiometric titration assembly.

In practice, one uses a standard reference calomel electrode, which consists of mercurous chloride ( $Hg_2Cl_2$ ) paste in contact with metallic mercury and  $KCl$  solution. One form of the calomel electrode is shown in the assembly of the electrolytic cell, Fig. 10. This electrode constitutes one of the half-cells of the system. The other half-cell consists of the beaker which contains the solution to be titrated and into which a second electrode is placed. This second electrode may be either (1) a standard hydrogen electrode, (2) a quinhydrone electrode or (3) a glass electrode. Since the hydrogen electrode is subject to variations and difficult to maintain, the preference, in practice, is given to the quinhydrone or glass electrode.

A quinhydrone electrode is made by saturating the solution to be titrated with quinhydrone and dipping into it an unplatinized platinum electrode. Quinhydrone is a mixture of quinone and hydroquinone and the potential of the electrode depends upon the hydrogen-ion concentration. This electrode has certain limitations and is being replaced by

the glass electrode, which consists of a glass membrane in contact with a silver-silver chloride electrode.

It has already been shown that the Nernst equation, when applied to the measurement of hydrogen-ion concentration, takes the form

$$E = 0.0591 \log C_{H^+}$$

or

$$pH = \frac{E}{0.0591}$$

In the cell consisting of the normal calomel electrode, as reference, and the hydrogen electrode in the solution whose  $pH$  is to be determined, the e.m.f. is

$$E = 0.280 - 0.0591 \log C_{H^+}$$

or

$$pH = \frac{E - 0.280}{0.0591}$$

the value 0.280 being the difference between a normal hydrogen and normal calomel electrode.

In an actual titration, the cell is connected with a potentiometer and standard solution is titrated into the half-cell containing the solution of the sample. The voltages,  $E$ , are noted as the titration progresses, the corresponding  $pH$  value calculated and plotted on graph paper. These titration curves are similar in shape to those shown previously and calculated from volume and normality relationship. The equivalence point is obtained by dropping a line from the vertical portion of the graph to the volume ( $x$ ) axis.

#### PROBLEM SET 4

##### EQUILIBRIUM CALCULATIONS IN NEUTRALIZATION REACTIONS

1. Calculate the H-ion concentration in solutions of the following monobasic acids, the molarity, or normality and degree of ionization being given.

(a) HCl	0.1 M or 0.1 N	94.8%	Ans. (a) $9.48 \times 10^{-2}$
(b) HNO <sub>2</sub>	0.1 M or 0.1 N	8.0%	(b) $8.0 \times 10^{-3}$
(c) HCHO	0.1 M or 0.1 N	4.5%	(c) $4.5 \times 10^{-3}$
(d) HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0.1 M or 0.1 N	1.34%	(d) $1.34 \times 10^{-3}$
(e) HCN	0.1 M or 0.1 N	0.01%	(e) $1.0 \times 10^{-5}$

2. Calculate the H-ion concentration of a 0.01 N solution of acetic acid which is 4.17 per cent ionized. What is the H-ion concentration of 0.01 N solution of HCl which is 99.8 per cent ionized?



3. Calculate the  $\text{OH}^-$ -ion and  $\text{H}^+$ -ion concentration of the following solutions of bases, the normality and degree of ionization being given.  $K_w = 1 \times 10^{-14}$ .

			$\text{OH}^-$	$\text{H}^+$
(a) NaOH	0.1 N	90.5%	<i>Ans.</i> $9.05 \times 10^{-2}$	$1.11 \times 10^{-13}$
(b) KOH	0.01 N	93.5%	$9.35 \times 10^{-3}$	$1.07 \times 10^{-12}$
(c) $\text{NH}_4\text{OH}$	0.001 N	11.7%	$1.17 \times 10^{-4}$	$8.55 \times 10^{-11}$

4. Calculate the  $\text{OH}^-$ -ion and  $\text{H}^+$ -ion concentrations in solutions of  $\text{NH}_4\text{OH}$  of the following normalities and degrees of ionization. ( $K_w = 1 \times 10^{-14}$ .)

(a) 1.0 N	0.4%
(b) 0.1 N	1.31%
(c) 0.01 N	4.07%
(d) 0.001 N	11.7%

5. For the following solutions, the  $\text{H}^+$ -ion concentrations of which are given, express the acidity in terms of pH values.

<i>Solution</i>	$C_{\text{H}^+}$	pH
(a) HCl	$9.48 \times 10^{-2}$	<i>Ans.</i> (a) 1.02
(b) $\text{HNO}_2$	$8.0 \times 10^{-3}$	(b) 2.1
(c) HCHO	$4.5 \times 10^{-3}$	(c) 2.35
(d) $\text{HC}_2\text{H}_3\text{O}_2$	$1.34 \times 10^{-3}$	(d) 2.87
(e) HCN	$1 \times 10^{-5}$	(e) 5.00

6. Find the pH values for the following bases having the  $\text{H}$ -ion concentration corresponding to the normalities given.

(a) NaOH	$1.11 \times 10^{-13}$	0.1 N
(b) KOH	$1.07 \times 10^{-12}$	0.01 N
(c) $\text{NH}_4\text{OH}$	$8.55 \times 10^{-11}$	0.001 N

7. Suppose that you mixed 20.00 ml. of 0.1 N NaOH with 30.00 ml. of 0.1 N HCl. What would be (a) the  $\text{H}$ -ion concentration, and (b) the pH value of the resulting mixture, assuming complete ionization?

*Ans.* (a)  $2 \times 10^{-2}$   
(b) 1.70

8. If to 25.00 ml. of 0.1 N NaOH you added 12.50 ml. of 0.1 N HCl, what would be (a) the  $\text{OH}$ -ion concentration, (b) the  $\text{H}$ -ion concentration and (c) the pH value of the resulting mixture, assuming complete ionization?

9. Calculate (a) the  $\text{H}$ -ion concentration and (b) the pH value of a 0.01 N solution of  $\text{NaC}_2\text{H}_3\text{O}_2$ .  $(C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-})/C_{\text{HC}_2\text{H}_3\text{O}_2} = 1.8 \times 10^{-5}$ ;  $C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$ .

*Ans.* (a)  $4.76 \times 10^{-9}$   
(b) 8.34

10. Calculate the pH value of a 0.01 N solution of  $\text{NH}_4\text{Cl}$ .  $(C_{\text{NH}_4^+} \times C_{\text{OH}^-})/C_{\text{NH}_4\text{OH}} = 1.75 \times 10^{-5}$ .  $C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$ .

11. Calculate the pH value of the mixture when 25.00 ml. of 0.1 N HCl are mixed with 75.00 ml. of 0.1 N  $\text{NH}_4\text{OH}$ .  $(C_{\text{NH}_4^+} \times C_{\text{OH}^-})/C_{\text{NH}_4\text{OH}} = 1.75 \times 10^{-5}$ .  $C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$ .

*Ans.* 9.48

12. What is the pH value of the mixture obtained by adding 50.00 ml. of 0.5 N NaOH to 50.00 ml. of 0.5 N  $\text{HC}_2\text{H}_3\text{O}_2$ ?  $(C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-})/C_{\text{HC}_2\text{H}_3\text{O}_2} = 1.8 \times 10^{-5}$ .  $C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$ .

13. Suppose you were titrating 25.00 ml. of 0.1  $N$   $\text{HC}_2\text{H}_3\text{O}_2$  with 0.1  $N$   $\text{NaOH}$ . (a) What would be the  $p\text{H}$  value of the acid before titration was begun (degree of ionization 1.3 per cent)? (b) What would be the  $p\text{H}$  of the solution when one half of the equivalent of  $\text{NaOH}$  (12.50 ml.) had been added? (c) When 0.9 of the acid is neutralized?

*Ans.* (a) 2.89  
(b) 4.74  
(c) 5.70

14. If you were titrating 50.00 ml. of 0.1  $N$   $\text{HCl}$  with 0.1  $N$   $\text{NaOH}$ , what would be the  $p\text{H}$  value (a) when 30.00 ml. of the  $\text{NaOH}$  solution were added, (b) when 47.50 ml.  $\text{NaOH}$  were added and (c) when 49.90 ml.  $\text{NaOH}$  were added? Assume complete ionization.

15. If, for convenience, we mix solutions of 0.1  $N$   $\text{NH}_4\text{OH}$  and 0.1  $N$   $\text{HCl}$  in such proportions that the total volume of solution is 100 ml., what will be the  $p\text{H}$  (a) when we mix 55.0 ml. acid and 45.0 ml. base; (b) when 50.0 ml. of each are mixed; and (c) when 40.0 ml. of acid are mixed with 60.0 of base?  $K_w = 1.2 \times 10^{-14}$ ;  $K_{\text{ion}} \text{NH}_4\text{OH} = 1.75 \times 10^{-5}$

*Ans.* (a) 4.0  
(b) 5.24  
(c) 8.88

16. If we mix solutions of 0.1  $N$   $\text{NaOH}$  and 0.1  $N$   $\text{HC}_2\text{H}_3\text{O}_2$  in the following proportions, what will be the  $p\text{H}$  values of the resulting mixtures? (a) 65.0 ml. acid and 35.0 ml. base; (b) 50.0 ml. of each; and (c) 10.0 ml. of acid and 90.0 ml. of base.  $K_w = 1.2 \times 10^{-14}$ .  $K_{\text{ion}} \text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$ .

17. Calculate the  $p\text{H}$  of the mixture when 12.50 ml. of 0.1  $N$   $\text{HCl}$  have been added to 25.00 ml. of 0.1  $N$   $\text{NH}_4\text{OH}$ .

*Ans.* 9.2

18. Imagine you are titrating 25.00 ml. of a 0.1  $N$   $\text{NH}_4\text{OH}$  solution with 0.1  $N$   $\text{HCl}$ . What are the  $p\text{H}$  values when (a) 5 per cent, (b) 60 per cent, (c) 90 per cent and (d) 99.9 per cent of the base have been neutralized?

19. If you mix equivalent volumes of a base, whose  $K_{\text{ion}}$  is  $1 \times 10^{-5}$ , with an acid, whose  $K_{\text{ion}}$  is  $1 \times 10^{-7}$ , what will be the  $\text{H-ion}$  concentration of the mixture?

*Ans.*  $1.1 \times 10^{-8}$

20. Calculate the hydrolysis constant for  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ .

## ADDITIONAL STOICHIOMETRIC CALCULATIONS

**Adjustment of Solutions.** (a) **ADJUSTMENT TO AN EXACT NORMALITY.** Solutions prepared and standardized for titration purposes are rarely of the exact strength desired. That is, they usually are of the approximate strength called for but, of course, their exact strength becomes known upon standardization and they are then used without further adjustment of concentration. It sometimes becomes necessary or desirable to adjust the concentration to some definite desired value by addition of water or solute. The exceptions to this are those solutions which can be made by weighing out an exact amount of primary standard.

For example, suppose that it is desired to change the strength of an  $\text{HCl}$  solution which is 0.1019  $N$  to one which is exactly 0.1000  $N$ . How much water must be added to 700 ml. of the 0.1019  $N$  hydrochloric acid solution in order to have one of the desired normality?



The diluted solution must contain 0.003647 gram of HCl per milliliter in order to be 0.1000 *N*. The undiluted solution contains  $0.03647 \times 0.1019$  or 0.003716 gram per milliliter; in 700 ml. there are  $0.003716 \times 700$  or 2.60 grams of HCl.

This quantity of pure HCl must be present in the total volume of diluted solution such that each milliliter contains 0.003647 gram of HCl. If  $x$  represents the volume of diluted solution, then

$$\begin{aligned} 0.003647 \times x &= 2.60 \\ x &= 713.3 \text{ ml.} \end{aligned}$$

Then  $713.3 - 700.0 = 13.3$  ml., the amount of water to be added.

Since the normality is inversely proportional to the volume, the volume of diluted solution,  $y$ , can also be directly calculated from the relation

$$\begin{aligned} 700 \text{ ml.} : y \text{ ml.} &= 0.1 : 0.1019 \\ y &= 713.3 \text{ ml.} \end{aligned}$$

and the volume of water to add is 13.3 ml.

Such calculations are made on the assumption that no shrinkage in the total volume takes place on mixing.

(b) ADJUSTMENT OF SOLUTIONS TO READ PERCENTAGE DIRECTLY. In many routine and industrial analyses it is desirable to adjust either the weight of sample or the strength of the titrating solution so that the volume of standard solution will indicate directly the percentage of the desired constituent or bear a simple relation to the percentage. The problem resolves itself into either finding how much solute is needed in making a solution for titrating a definite weight of sample so that each milliliter of solution used in titrating the sample will represent 1 per cent of the desired constituent, or else fixing the weight of sample that must be taken so that with a specified strength of the solution the volume used will represent 1 per cent of the desired constituent. The following case will serve as an example.

How much HCl must be contained in a milliliter of solution so that, with a 1-gram sample of impure  $\text{Na}_2\text{CO}_3$ , each milliliter used in titrating the sample represents 1 per cent of  $\text{Na}_2\text{CO}_3$ ?

From the equation

$$\frac{1 \text{ ml.} \times \text{Na}_2\text{CO}_3 \text{ titer of the HCl solution}}{1 \text{ gram}} \times 100 = 1 \text{ per cent}$$

we have

$$\frac{1 \times 0.01}{1} \times 100 = 1 \text{ per cent}$$

The value of 1 ml. of the solution in terms of  $\text{Na}_2\text{CO}_3$  is therefore 0.01. Then  $(2\text{HCl}/\text{Na}_2\text{CO}_3) \times 0.01 =$  value of 1 ml. in terms of HCl and equals 0.00688 gram. A liter of this solution must contain 6.88 grams of HCl.

If a 2-gram sample is used, and each milliliter is to indicate 1 per cent, the strength of the solution must be twice as great.

Instead of adjusting the strength of the solution, which is a tedious matter experimentally, the weight of sample may be adjusted so that, with a solution of given strength, the volume of solution used represents directly the percentage of the desired constituent.

What weight of sample of soda ash should be taken so that, when titrated with a hydrochloric acid solution having an HCl titer of 0.01820, each milliliter should represent exactly 1 per cent of  $\text{Na}_2\text{CO}_3$ ?

Since

$$\frac{1 \text{ ml.} \times 0.01820 \times \frac{\text{Na}_2\text{CO}_3}{2\text{HCl}}}{\text{Weight of sample}} \times 100 = 1 \text{ per cent}$$

the weight of sample is found to be 2.645 grams.

The same adjustments may be made on a normality basis.

What must be the normality of a hydrochloric acid solution so that, when a 2.000-gram sample of soda ash is titrated, each milliliter of HCl represents 1 per cent of  $\text{Na}_2\text{CO}_3$ ? From the general relation:

$$\frac{\text{Volume used} \times \text{Normality} \times \text{Milliequivalent weight}}{\text{Weight of sample}} \times 100 = \text{Percentage}$$

we have

$$\frac{1 \text{ ml.} \times N \times \frac{\text{Na}_2\text{CO}_3}{2 \times 1000}}{2.000} \times 100 = 1 \text{ per cent}$$

from which  $N = 0.3773$ .

What weight of soda ash must be taken in order that the volume of a 0.500  $N$  HCl solution should represent the percentage of  $\text{Na}_2\text{CO}_3$ ?

$$\frac{1 \text{ ml.} \times 0.500 \times 0.0530}{\text{Weight of sample}} \times 100 = 1 \text{ per cent}$$

from which the weight of sample required is 2.65 grams.

**Calculations of Mixed Alkalies.** In the usual method of calculating the alkaline strength of a basic material, the total alkalinity is computed in terms of the percentage of the constituent which predominates. For



example, in the analysis of soda ash, which is largely  $\text{Na}_2\text{CO}_3$  but, besides inert material, usually contains small amounts of  $\text{NaHCO}_3$ , the result is reported as percentage of  $\text{Na}_2\text{CO}_3$ , whereas in reality both alkaline substances react with the acid used for neutralization. In cases of mixed alkalis, such as mixtures of the alkali hydroxides, carbonates and bicarbonates, the separate amounts of each constituent may be determined by titrations involving the use of two indicators.

The following possibilities may occur with the above alkalis using the sodium compounds as typical in samples which may also contain inert impurities such as chlorides and sulfates:

1.  $\text{NaOH}$  as the only alkaline substance.
2.  $\text{NaHCO}_3$  as the only alkaline substance.
3.  $\text{Na}_2\text{CO}_3$  as the only alkaline substance.
4. Mixtures of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .
5. Mixtures of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ .

Besides these, we may have dry mixtures of  $\text{NaOH}$  and  $\text{NaHCO}_3$  or dry mixtures of  $\text{NaOH}$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ , but these mixtures cannot exist in solutions because the hydroxide will react with the bicarbonate to form the carbonate. Samples covering the above five cases can be identified and the percentages of the constituents determined by the behavior of methyl orange and phenolphthalein indicators toward these alkalis during titration.

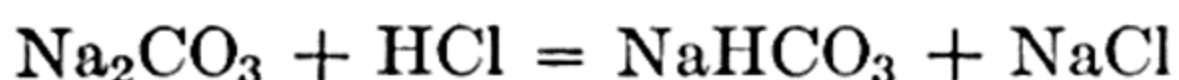
1. **SODIUM HYDROXIDE.** This base behaves alike toward both indicators so that, when a titration is conducted with standard  $\text{HCl}$ , the end point comes at practically the same volume of added acid when methyl orange is used as when phenolphthalein is used. Complete neutralization is indicated when methyl orange turns pink and phenolphthalein turns colorless.

2. **SODIUM BICARBONATE.** This base is practically neutral toward phenolphthalein. This is because the hydrogen-ion concentration derived from the weakly ionized  $\text{HCO}_3^-$  ion ( $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{=}$ ) has about the concentration ( $1 \times 10^{-9}$ ) necessary to change the color of this indicator, so that a minute amount of  $\text{HCl}$  is sufficient to indicate a neutral solution when phenolphthalein is present.

Methyl orange, however, does not change color from alkaline to acid until a concentration of hydrogen ion of about  $1 \times 10^{-4}$  is reached. This will occur only when the bicarbonate is actually neutralized. A titration of bicarbonate with standard acid can therefore be made only with methyl orange as indicator.

3. **SODIUM CARBONATE.** With phenolphthalein present, *in a cold solution*, a titration of sodium carbonate with standard  $\text{HCl}$  will show an

end point when the solution is only one-half neutralized, that is, when the  $\text{Na}_2\text{CO}_3$  has been transformed into  $\text{NaHCO}_3$ , thus:



The volume of acid used will therefore be one-half of the total amount required for complete neutralization.

With methyl orange the end point does not come until complete neutralization takes place.

4. A MIXTURE OF  $\text{NaOH}$  AND  $\text{Na}_2\text{CO}_3$ . Remembering from the foregoing cases that methyl orange changes color at complete neutralization for any alkali and that phenolphthalein shows a neutral reaction against  $\text{NaHCO}_3$ , the behavior of the above mixture can be easily deduced. When the mixture is titrated with acid, in the cold, in the presence of phenolphthalein as indicator, all the  $\text{NaOH}$  and one-half of the  $\text{Na}_2\text{CO}_3$  will have been neutralized when the pink color is discharged. A second titration, using methyl orange, will give the total volume of acid required for complete neutralization of both bases. The following problem will show the method of calculation.

A 0.2-gram sample of a mixture of  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and impurities was dissolved in water and then titrated cold with 0.1  $N$   $\text{HCl}$ , using phenolphthalein as indicator. The volume of acid required was 30.00 ml. Another 0.2-gram sample of the mixture was taken, dissolved in water and titrated with 0.1  $N$   $\text{HCl}$ , using methyl orange as indicator. This second titration required 40.00 ml. of the acid. What were the percentages of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  in the sample?

Since the total volume of acid required for complete neutralization of both compounds was 40.00 ml. and the volume required for the complete neutralization of  $\text{NaOH}$  plus the neutralization of one-half of the  $\text{Na}_2\text{CO}_3$  was 30.00 ml., the difference in volume between the first and the second titration was 10 ml., which represents the volume required for one-half of the  $\text{Na}_2\text{CO}_3$ . Therefore the volume required for the complete neutralization of the  $\text{Na}_2\text{CO}_3$  is 20 ml., and the volume required for the complete neutralization of the  $\text{NaOH}$  is likewise 20 ml. The milliequivalent weight of  $\text{NaOH}$  is 0.04000, and the milliequivalent weight of  $\text{Na}_2\text{CO}_3$  is 0.0530.

Therefore

$$\frac{20.00 \text{ ml.} \times 0.1 \times 0.04000}{0.2000} \times 100 = 40.00 \text{ per cent of NaOH}$$

and

$$\frac{20.00 \text{ ml.} \times 0.1 \times 0.0530}{0.2000} \times 100 = 53.00 \text{ per cent of Na}_2\text{CO}_3$$



5. MIXTURE OF  $\text{Na}_2\text{CO}_3$  AND  $\text{NaHCO}_3$ . If a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  is titrated with acid, using phenolphthalein indicator in a cold solution, the end point will come when one-half of the  $\text{Na}_2\text{CO}_3$  is neutralized; this is equivalent to the transformation of all the carbonate into bicarbonate. The bicarbonate originally present, as well as that formed from the carbonate, will be neutral toward this indicator. A second titration, in the presence of methyl orange, will give an end point when both compounds are completely neutralized.

As an example, suppose that a 0.2-gram sample of a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and inert material was titrated with 0.1 *N* HCl, using phenolphthalein as indicator. The volume of acid required was 10.00 ml. When the sample was titrated with methyl orange indicator the volume of 0.1 *N* HCl required for complete neutralization was 30.00 ml.

Since in the first titration the  $\text{Na}_2\text{CO}_3$  was half neutralized and none of the bicarbonate reacted with the acid, the volume of acid required for complete neutralization of the  $\text{Na}_2\text{CO}_3$  is  $2 \times 10.00$  or 20.00 ml. In the second titration, since a total of 30.00 ml. of acid was required and 20.00 ml. of this was used by the  $\text{Na}_2\text{CO}_3$  the volume required for the  $\text{NaHCO}_3$  was 10.00 ml. The milliequivalent weight of  $\text{Na}_2\text{CO}_3$  is 0.0530, and that of  $\text{NaHCO}_3$  is 0.0840. Therefore

$$\frac{20.00 \text{ ml.} \times 0.1 \times 0.0530}{0.2000} \times 100 = 53.00 \text{ per cent of } \text{Na}_2\text{CO}_3$$

and

$$\frac{10.00 \text{ ml.} \times 0.1 \times 0.0840}{0.2000} \times 100 = 42.00 \text{ per cent of } \text{NaHCO}_3$$

*Volume Relationships.* The relationships in the volumes of acid used may be summarized as follows:

<i>Volume Relation</i>	<i>Substance</i>
Same volume for both indicators	$\text{NaOH}$
No volume for P.P.	$\text{NaHCO}_3$
Twice the volume for M.O. as for P.P.	$\text{Na}_2\text{CO}_3$
More than half the total volume for P.P.	$\text{NaOH}$ and $\text{Na}_2\text{CO}_3$
Less than half the total volume for P.P.	$\text{NaHCO}_3$ and $\text{Na}_2\text{CO}_3$

The important fact, which is the key to the solution of mixed alkali and double indicator problems, is that *phenolphthalein is neutral to bicarbonates* when used in a cold solution.

## PROBLEM SET 5

## ADJUSTMENT OF STRENGTH AND MIXED ALKALI CALCULATIONS

## (a) Adjustment

1. What volume of concentrated HCl (sp. gr. 1.19, containing 37.23 per cent of HCl by weight) must be added to 500 ml. of 0.10 *N* HCl in order to make it 0.20 normal? *Ans.* 4.2 ml.

2. What volume of 0.5123 *N* H<sub>2</sub>SO<sub>4</sub> must be added to 500 ml. of 0.4961 *N* HCl in order to make a solution which is exactly 0.5000 *N*?

3. How many grams of NaOH must be added to 1 liter of HCl, 1 ml. of which will react with 0.004150 gram of NaOH in order to make it 0.1000 normal? *Ans.* 0.1480 gram

4. What weight of sample of pearl ash (impure K<sub>2</sub>CO<sub>3</sub>) should be taken for analysis in order that the volume of HCl used (1 ml. = 0.01500 gram K<sub>2</sub>CO<sub>3</sub>) will give the per cent of K<sub>2</sub>CO<sub>3</sub>?

5. What weight of sample of H<sub>2</sub>SO<sub>4</sub> should be used so that the per cent of SO<sub>3</sub> should equal one-half the volume of 0.1 *N* NaOH used? *Ans.* 0.80 gram

6. How many grams of pure NaOH per liter should a solution of NaOH contain so that, when neutralizing a 1.5000-gram sample of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, the volume will represent twice the per cent of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> present?

7. Suppose 500 ml. of 0.4678 *N* NaOH are mixed with 500 ml. of 0.5473 *N* NaOH. What is the normality of the resulting mixture, assuming 1 liter of mixture? How much water must be added to a liter of this mixed solution in order to make it 0.5 *N*? *Ans.* 0.5076 *N*; 15 ml.

8. What weight of soda ash should be taken for analysis so that, when titrated with 0.1258 *N* HCl solution, the volume of acid required will equal directly the percentage of Na<sub>2</sub>CO<sub>3</sub> in the sample?

9. In the determination of NaOH in commercial caustic soda by titration with 0.5000 *N* HCl, what should the weight of sample be so that the percentage of NaOH is twice the number of milliliters of HCl used? *Ans.* 1.0000 gram

10. A sample of caustic soda was found to be 50 per cent pure. What is the maximum weight of sample that can be titrated with 0.3750 *N* HCl without refilling a 50-ml. buret?

## (b) Mixed Alkalies

11. (a) What volume of 0.100 *N* HCl will be required to titrate a 0.2500-gram sample of pure Na<sub>2</sub>CO<sub>3</sub> using phenolphthalein in a cold solution? (b) What volume is required to titrate the same weight of sample using methyl orange? *Ans.* (a) 23.6 ml.  
(b) 47.2 ml.

12. How many milliliters of 0.100 *N* HCl are required to titrate a 0.2500-gram mixture of equimolecular quantities of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> using (a) phenolphthalein and (b) methyl orange as indicator?

13. How many milliliters of 0.1000 *N* HCl are required to titrate a 0.2500-gram mixture of equal parts by weight of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> using (a) phenolphthalein and (b) methyl orange as indicator? *Ans.* (a) 11.78 ml.  
(b) 38.43 ml.



14. An impure NaOH sample required 30.00 ml. of 0.200 *N* HCl for titration to the phenolphthalein end point and an additional 3.00 ml. of acid to carry the titration from the phenolphthalein to the methyl orange end point. How many grams of NaOH and Na<sub>2</sub>CO<sub>3</sub> were present in the sample?

15. Calculate the percentages of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> in a 1.4000-gram sample which, on titrating with 0.1234 *N* HCl using phenolphthalein, required 15.25 ml. and, on titrating the same weight with the standard acid using methyl orange, required 37.28 ml.

*Ans.* 14.25 per cent; 5.02 per cent

16. An alkali sample was found to contain 92 per cent NaOH and 6 per cent Na<sub>2</sub>CO<sub>3</sub>. Find the normality (*a*) with respect to the phenolphthalein titration and (*b*) with respect to the methyl orange titration if 5.00 grams of the alkali were dissolved and diluted to exactly 1 liter.

17. A sample is known to contain NaOH and Na<sub>2</sub>CO<sub>3</sub>. If a 0.3000-gram sample containing 35.00 per cent NaOH requires 33.25 ml. of 0.1000 *N* HCl for titration to the phenolphthalein end point, what volume of HCl will be required to complete the titration to the methyl orange end point?

*Ans.* 7.00 ml.

18. A sample of impure NaHCO<sub>3</sub> weighing 1.5000 grams required 9.93 ml. of 0.1522 *N* HCl for a phenolphthalein titration. A 1.2420-gram sample required 43.72 ml. of 0.1522 *N* HCl for a methyl orange titration. Calculate the percentages of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>.

19. A mixture is known to consist of equivalent amounts of NaOH and Na<sub>2</sub>CO<sub>3</sub>, or of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. If the volumes of acid required for methyl orange and phenolphthalein titrations are approximately in the ratio of 4 : 3, which mixture is present?

*Ans.* NaOH and Na<sub>2</sub>CO<sub>3</sub>

20. A 1.00-gram sample of equal parts of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> was titrated using phenolphthalein as indicator. Another 1.00-gram sample was titrated using methyl orange. What volume of 0.556 *N* H<sub>2</sub>SO<sub>4</sub> was required in each titration?

## CHAPTER IV

### OXIDATION AND REDUCTION METHODS

#### GENERAL CONSIDERATIONS

The reactions between oxidizing and reducing substances comprise the largest group of volumetric methods of analysis. Many excellent and very accurate methods for the determination of a large number of substances are based on reactions between oxidizing and reducing agents. Before considering such methods in detail it will be well to review the general nature of the phenomena of oxidation and reduction and briefly consider the electrochemical aspects of the subject.

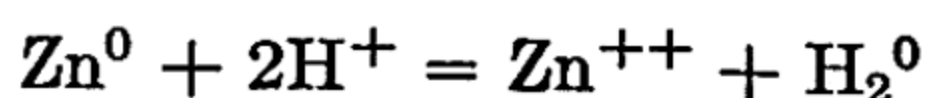
**Nature of Oxidation and Reduction.** The earliest notions relative to the phenomena of oxidation and reduction regarded such actions as direct additions of oxygen and of hydrogen. Later these ideas were modified to include the addition of elements other than oxygen, such as sulfur or the halogens, as true oxidations. Still later we have come to regard an oxidation as an increase in positive charges or a decrease in negative charges associated with ions and atoms, and a reduction as a decrease in positive charges or an increase in negative charges. For example, when iron changes from the ferrous to the ferric condition, there is an increase in the number of positive charges from  $+2$  to  $+3$ ; this is an oxidation. When stannic tin,  $\text{Sn}^{++++}$ , is changed to stannous tin,  $\text{Sn}^{++}$ , there is a decrease in the number of positive charges associated with the tin atom; this is a reduction.

**Oxidation and Reduction in Terms of Valence and Electron Transfers.** An increase in the number of positive charges is the result of the loss of electrons by an atom, a radical or an ion. A gain of electrons results in a net decrease of positive charges. The excess or deficiency of electrons associated with an atom may be regarded as its valence. The ferrous ion,  $\text{Fe}^{++}$ , for example, has an excess of two positive charges; it has resulted from a neutral atom of iron losing two electrons, and its valence is said to be  $+2$ . When a substance loses electrons, its positive valence is increased or its negative valence is decreased. Conversely, when a substance gains electrons, its positive valence is decreased or its negative valence is increased. Since an increase in positive valence

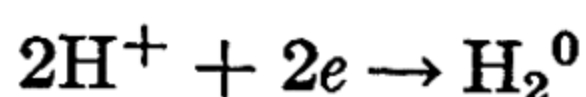
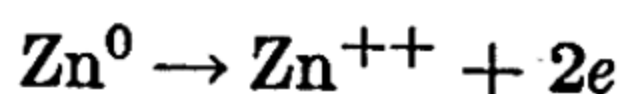


is an oxidation and a decrease in positive valence is a reduction and the valence change results from a loss or a gain of electrons, the term oxidation means a decrease in the number of electrons associated with the ion. Reduction, likewise, in terms of electrons, means a gain in the number of electrons by an ion. In the broadest sense, then, oxidation means the loss of one or more electrons and reduction means the gain of one or more electrons. In every reaction in which there is a transfer of electrons from one kind of atom to another, the electrons lost by atoms of one element must be gained by atoms of another element. That is, when one element is oxidized, another element is reduced.

Thus, in the reaction of metallic zinc with sulfuric acid, the change of valence is shown by writing the equation in ionic form, as:



in which the neutral zinc atom with zero valence becomes oxidized to the divalent, positively charged zinc ion, while two hydrogen ions are reduced to zero valence, becoming a molecule of gaseous hydrogen. The same change expressed in terms of electrons transferred from the zinc to the hydrogen may be shown by the electron or "half-cell" equations



in which the symbol  $e$  is used to denote an electron. The equations show that the total number of electrons lost by the zinc are taken up by the hydrogen. This reaction is thus truly one of oxidation-reduction. For an element or ion to function as an oxidizing agent it must readily accept electrons from the reducing agent, which in turn must easily lose one or more of its electrons. The word *redox* has recently come into use to designate such chemical changes, the word itself being derived by contracting the expression *reduction-oxidation*.

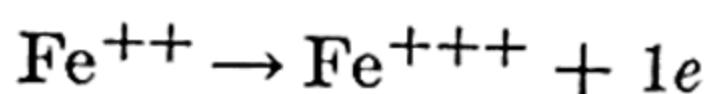
Since oxidation involves a loss of electrons and reduction a gain of electrons, the phenomena of oxidation and reduction are fundamentally electrical in nature. A reducing agent is a substance which is capable of losing electrons, being oxidized thereby; an oxidizing agent accepts electrons, becoming itself reduced. The transfer of electrons in oxidation-reduction reactions is therefore from the reducing agent to the oxidizing agent. When such reactions are made to take place by mixing a solution of an oxidizing agent with a solution of a reducing agent, as in titration procedures, the transfer of electrons is direct in the solution passing from the reducing ions to the oxidizing

ions. If, moreover, the oxidizing solution is placed in one beaker and the reducing solution in another, and the two solutions are joined by means of an inverted U-tube filled with an electrically conducting solution such as saturated KCl, and a wire conductor with metallic (usually platinum) electrodes used to complete the external circuit between the two beakers, electrons will flow through the wire from the reducing solution to the oxidizing solution and the same ultimate result is obtained as by mixing the two solutions.

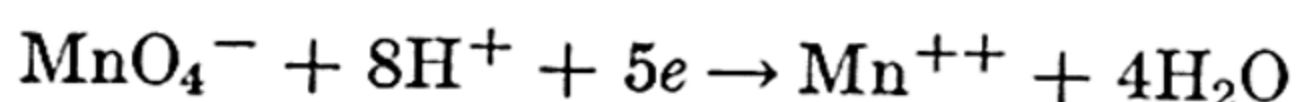
The flow of electrons constitutes an electric current, and the above-described arrangement is, in fact, an electrolytic cell. The production of an electric current, by chemical means, is essentially based on a redox reaction. Conversely, an electric current may be used, as in electroanalysis, to bring about reduction and deposition of metals and oxidation of anions at the two poles of an electrolyzing apparatus.

A strong oxidizing agent readily accepts electrons; a strong reducing agent easily gives up electrons. The relative ease with which a substance accepts or loses electrons is a measure of its relative oxidizing or reducing power. It is important to know how a strong oxidizing or reducing agent can be distinguished from a weak one. The tendency to gain or lose electrons can be measured, relatively, by electrochemical means. The method used is somewhat too complicated to discuss fully here and is only briefly outlined on page 104 under "Electrochemical Theory of Oxidation."

**Oxidizing and Reducing Ions.** Although these relations between metals or ions are examples of true oxidations and reductions, the relations between two species of ions of the same element in two states of oxidation are of much greater importance in quantitative analysis, because the oxidizing and reducing agents commonly used in titration procedures are of the variable-valence type. For example, when a ferrous salt solution is used as a reducing agent, the half-cell or electron reaction is



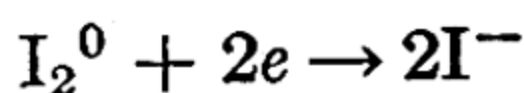
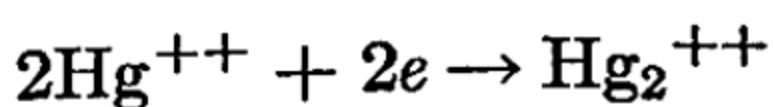
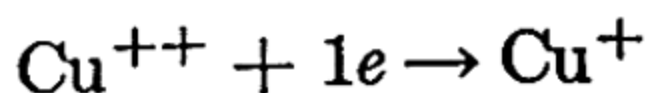
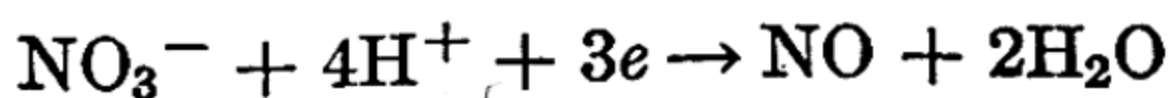
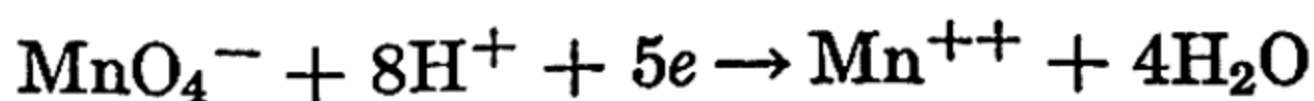
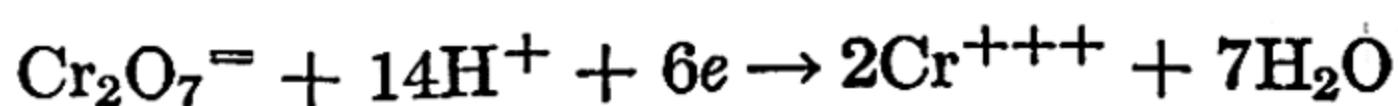
and the equilibrium ratio of ferrous- to ferric-ion concentration is an important consideration. Or, again, when  $\text{KMnO}_4$  is used as oxidizing agent in an acid medium, the relation between the oxidized and reduced forms is shown by the reaction



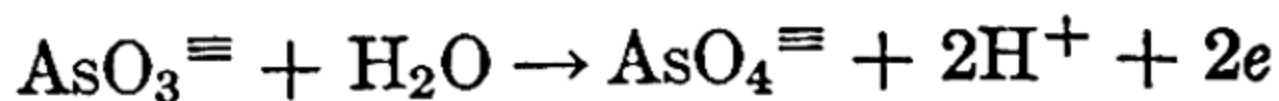
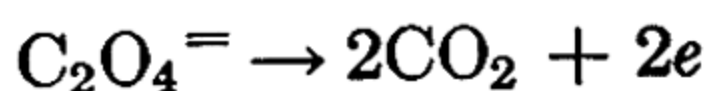
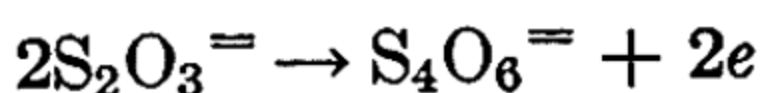
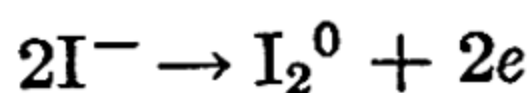
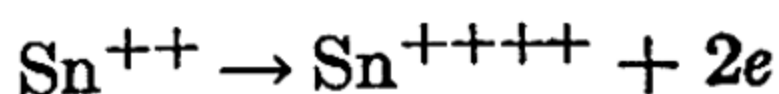
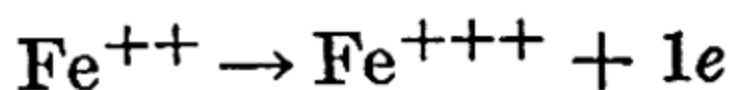
Here the ratio of  $\text{MnO}_4^-$  to  $\text{Mn}^{++}$ , i.e., the amount of  $\text{MnO}_4^-$  remaining unreduced when equilibrium is reached is, in part, a measure of the oxidizing power of permanganate.



The relation between the two forms of a few commonly used oxidizing agents is shown below, in the form of reactions between the two species of ions.

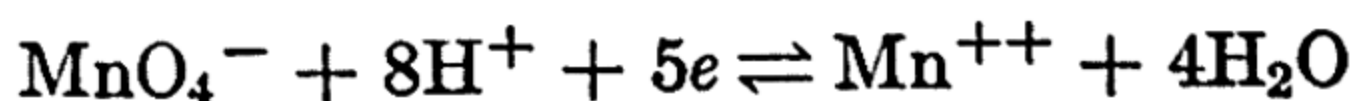


Likewise, the two forms of ions of a few typical reducing agents are shown below.

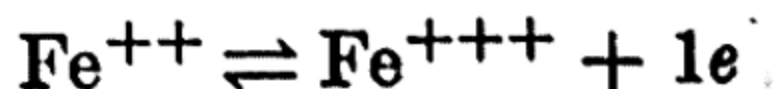


Further examples are given in the table on page 108.

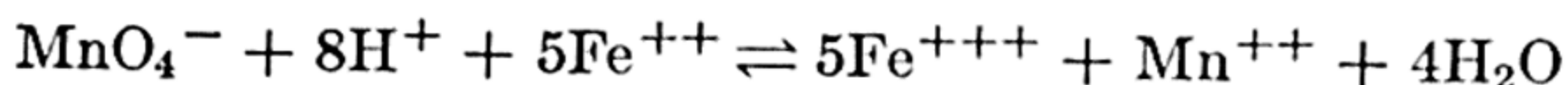
These half-cell reactions cannot proceed of their own accord because some means must be provided for furnishing the necessary electrons for the oxidizing agents and of getting rid of the electrons for the reducing agents. In order that reactions can take place, suitable oxidizing and reducing agents must be brought together. The final equilibrium reached in the reaction as a whole will then depend upon the equilibrium ratios of both pairs. Thus to promote the reaction



so that, when equilibrium is reached, the solution should contain negligible amounts of the  $\text{MnO}_4^-$  ion, a suitable reducing agent, such as a ferrous salt, is used. When the reaction

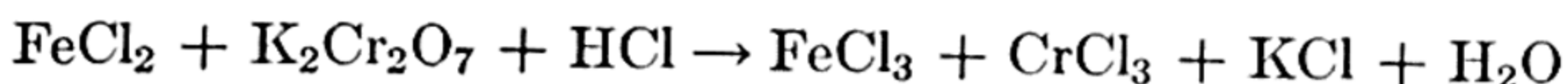


is combined with that for permanganate, i.e., when  $\text{MnO}_4^-$  is allowed to oxidize ferrous ion, the reaction



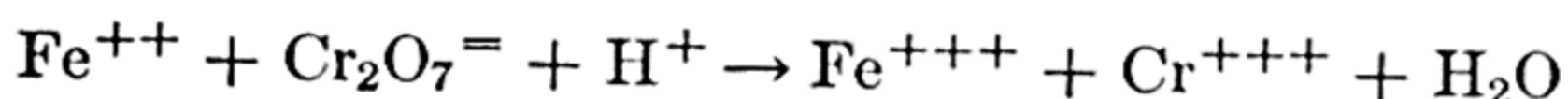
runs practically to completion.

**Balancing Equations of Oxidation-Reduction by Valence Changes.** The method of writing and balancing equations involving valence changes has been illustrated above for the simple case of the reaction of metallic zinc with sulfuric acid. A more complicated example will now be considered, namely, the oxidation of ferrous chloride by potassium dichromate in an acid solution. The reaction involved, written in unbalanced molecular form, is

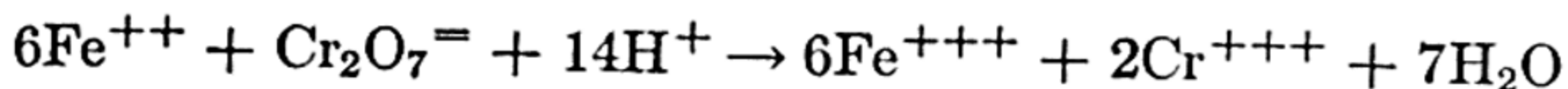


showing that the ferrous chloride is oxidized to the ferric (trivalent) condition, whereas the chromium in the potassium dichromate is reduced to the chromic (trivalent) condition, the oxygen of the dichromate uniting with the hydrogen of the acid to form water.

In ionic form, this unbalanced equation becomes



The chromium atom in the dichromate ion has a valence of six; in the chromic state it has a valence of three; each chromium atom suffers a reduction of three positive valences. Since there are two atoms of chromium in each dichromate ion, each atom of which loses three positive charges, the total loss will be six for each dichromate radical. The six charges lost by one  $\text{Cr}_2\text{O}_7^{=}$  ion must be accounted for by the gain of charges on the iron. Since each ferrous ion shows an increase of one positive valence on becoming a ferric ion, the six charges from one dichromate ion are assumed by six ferrous ions. Finally the seven atoms of oxygen from the dichromate ion require fourteen atoms of hydrogen from the acid to form seven molecules of water. The balanced equation in ionic form can now be written.



**Balancing Equations of Oxidation-Reduction by Electron Transfers.** Since change of valence means an exchange of electrons between the reducing agent and the oxidizing agent, the writing and balancing of oxidation-reduction reactions by the electron transfer method involves merely an extension of the above method. Thus, to take the same



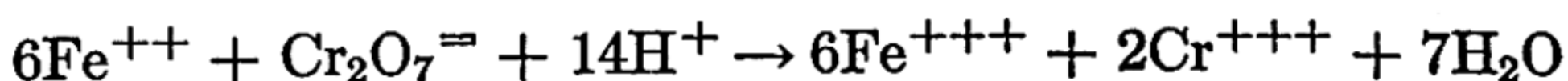
example, since each atom of chromium, in being reduced from the hexavalent to the trivalent state, gains three electrons, and two atoms of chromium are involved in each dichromate ion, the total gain of electrons for one  $\text{Cr}_2\text{O}_7^{=}$  ion is six:



The electrons gained by the chromium atoms are lost by ferrous ions, which in turn are oxidized to the ferric state. Since each ferrous ion gives up one electron, six ferrous ions are involved:

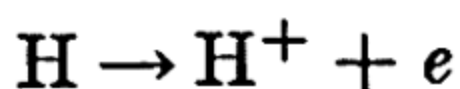


The number of hydrogen ions furnished by the acid is determined, as before, from the number of oxygen atoms available; seven oxygen atoms require fourteen hydrogen atoms and yield  $7\text{H}_2\text{O}$ . The balanced equation can then be written by assembling the electron equations, and the final equation becomes



In general, when setting up and balancing equations by this method, first write the unbalanced equation in ionic form; second, determine the number of electrons gained by the one element, which must equal the number of electrons lost by the element undergoing oxidation; third, assemble the separate electron equations and prefix the proper coefficient to each set of ions, thus giving the balanced ionic equation.

**Equivalent Weights and Normal Solutions.** A gram-equivalent weight is defined as that weight of substance which will involve, directly or indirectly, 1.008 grams of hydrogen. When an atom of hydrogen is oxidized to hydrogen ion, an electron is given up:



and this means that the gram-equivalent weight, 1.008 grams, of hydrogen is associated with one electron transfer. Hence for oxidizing and reducing substances, to be equivalent to this, the gram-atomic or gram-molecular weight is divided by the number of electrons lost or gained. This corresponds to the change in valence.

**Electrochemical Theory of Oxidation-Reduction.** A metal such as zinc placed in a solution of its ions shows a greater tendency to pass into solution than to deposit the zinc ions. Conversely, cupric ions show a greater tendency to deposit than for metallic copper to dissolve. The tendency to dissolve is known as solution pressure and the reverse

tendency as osmotic pressure. Whether a metal will dissolve in a dilute solution of its ions or come out of solution depends upon the relative magnitudes of its solution pressure and osmotic pressure. If the electrolytic solution pressure is greater than the osmotic pressure, a certain amount of the metal will pass into solution and assume the ionic state. If the osmotic pressure is the greater, metal ions will be deposited; and if both pressures are equal the metal ions will form at the same rate at which metal atoms are deposited. When equilibrium is reached obviously the two opposing effects are the same.

If positively charged ions are forming at a greater rate than the ions are being deposited, the strip of metal will assume a negative charge and the solution in contact with it will be positively charged. There will thus be set up a potential difference between the metal and its ions. The greater the concentration of ions the greater this potential difference. If ions are losing their positive charges faster than they are being formed, the metal strip will be positively charged and the solution negatively charged. At equilibrium, the rates in both directions are equal and the difference of potential becomes constant.

**The Nernst Equation.** The potential difference set up at the contact between a metal and a solution of its ions is related to the osmotic pressure of the solution and the electrolytic solution pressure of the metal by an equation first formulated by Nernst. The Nernst equation is

$$E = \frac{RT}{nF} \log_e \frac{p}{P}$$

where  $E$  = potential difference between the metal and its ions  
 $R$  = the gas constant = 8.32 joules per degree  
 $T$  = absolute temperature ( $273 + t^{\circ}\text{C.}$ )  
 $n$  = valence change (number of electrons lost or gained per atom)  
 $F$  = one Faraday or 96,500 coulombs  
 $\log_e$  = the natural logarithm to the base  $e$   
 $p$  = osmotic pressure  
 $P$  = electrolytic solution pressure.

This equation can be transformed into a more usable one. By inserting the values for  $R$  and  $F$  and converting natural logarithms into common logarithms to the base 10 by multiplying by 2.303, the equation becomes

$$E = \frac{0.000198T}{n} \log_{10} \frac{p}{P}$$



for any absolute temperature  $T$ . For the temperature of  $25^{\circ}\text{C}$ . or  $298^{\circ}$  absolute, we have

$$E = \frac{0.059}{n} \log_{10} \frac{p}{P}$$

If the equilibrium concentration of ions,  $k$ , is substituted for  $p$ , and  $p$  is expressed in terms of the ionic concentration,  $C$ , since osmotic pressure is proportional to the concentration, the Nernst equation becomes

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

**Measurement of Electrode Potentials.** There is no direct way by which the potential difference at the contact of a metal and a solution of its ions can be determined, but relative values can be obtained by setting up a voltaic cell in which one electrode is arbitrarily taken as the standard and the other electrode as the one whose potential is desired. Two such standard electrodes are in use. One is the normal hydrogen electrode, in which a platinum foil coated with platinum black is immersed in a solution of acid,  $1\ M$  with respect to hydrogen ions, the solution and electrode being kept saturated with hydrogen gas. The potential of the hydrogen electrode is arbitrarily taken as zero.

The other standard is the calomel electrode. This consists of mercury covered with a layer of calomel paste ( $\text{Hg}_2\text{Cl}_2$ ) which in turn is covered with a solution of  $\text{KCl}$  saturated with  $\text{Hg}_2\text{Cl}_2$ .

If then we wish to measure the potential of a metal in contact with a certain concentration of its ions, the metal and a solution of its ions are made a half-cell of a voltaic cell, the other half-cell being a standard hydrogen or calomel electrode. The two half-cells are joined by a U-tube filled with a conducting solution such as  $\text{KCl}$ , and the electrical circuit is completed by joining the electrodes to a sensitive voltmeter or potentiometer. The voltage measured is that of the cell as a whole. The potential of the electrode is the algebraic difference of the observed voltage and that of the standard electrode.

**Molar Electrode Potentials.** The potential of any metal in contact with its ions varies with the concentration of the ions. In order to arrange the metals in a series with respect to their relative potentials, the potentials are compared for unit gram-ion concentration of their ions, that is, for solutions containing  $1$  gram-ion per liter of the metal ion. Metal electrodes dipping into  $1\ M$  solutions of their salts would give this concentration of metallic ions, if such molar solutions were completely ionized. In the actual determination of molar potentials, the metal is

made the electrode in a solution much more dilute, 0.01 or 0.001  $M$ , and the potential for a 1  $M$  solution is then calculated from the Nernst equation.

The Nernst equation

$$E = \frac{0.059}{n} \log \frac{C}{k} \quad (1)$$

may be expanded into the form

$$E = \frac{0.059}{n} \log \frac{1}{k} + \frac{0.059}{n} \log C \quad (2)$$

If the concentration of the metal ion is 1  $M$ , the molar potential, usually designated by the symbol  $E_0$ , is expressed by the equation

$$E_0 = \frac{0.059}{n} \log \frac{1}{k}$$

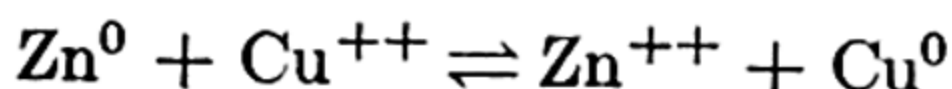
By substituting  $E_0$  for  $0.059/n \log 1/k$ , the Nernst equation for the electrode potential,  $E$ , for any concentration,  $C$ , of metal ion becomes

$$E = E_0 + \frac{0.059}{n} \log C \quad (3)$$

From this, by measuring the electromotive force of a cell, using the hydrogen electrode as reference to which the value of 0 is arbitrarily assigned, the molar potential,  $E_0$ , can be obtained by direct calculation from equation 3.

In this way the values of  $E_0$  have been obtained and arranged in the familiar electromotive series of the metals. By methods somewhat more complicated, the molar potentials of most oxidizing and reducing ions have been measured. These molar potentials are shown in Table VII.

**Calculation of Equilibrium Constants for Reactions in Which One Metal Replaces Another from Solution.** A strip of zinc placed in a solution of a copper salt will cause the deposition of metallic copper, some of the zinc going into solution as zinc ions. The reaction taking place is



in which the metallic zinc,  $\text{Zn}^0$ , is the reducing agent and the copper ions,  $\text{Cu}^{++}$ , the oxidizing agent.

The Law of Chemical Equilibrium, when applied to this reaction, takes the form

$$\frac{C_{\text{Zn}^{++}} \times C_{\text{Cu}^0}}{C_{\text{Cu}^{++}} \times C_{\text{Zn}^0}} = K$$



TABLE VII. STANDARD OXIDATION-

Oxidizing Potential Referred to Normal Hydrogen Electrode = 0	Reaction
*	$\text{BiO}_3^- + 6 \text{H}^+ + 2e = \text{Bi}^{+++} + 3 \text{H}_2\text{O}$
*	$\text{IO}_4^- + 2 \text{H}^+ + 2e = \text{IO}_3^- + \text{H}_2\text{O}$
*	$1/2 \text{S}_2\text{O}_8^{--} + e = \text{SO}_4^{--}$
1.82	$\text{Co}^{+++} + e = \text{Co}^{++}$
1.78	$1/2 \text{H}_2\text{O}_2 + \text{H}^+ + e = \text{H}_2\text{O}$ (action toward reducing agents)
1.68	$\text{PbO}_2 + 4 \text{H}^+ + \text{SO}_4^{--} + 2e = \text{PbSO}_4 + 2 \text{H}_2\text{O}$
1.59	$\text{MnO}_4^- + 4 \text{H}^+ + 3e = \text{MnO}_2 + 2 \text{H}_2\text{O}$
1.5	$\text{MnO}_4^- + 8 \text{H}^+ + 5e = \text{Mn}^{++} + 4 \text{H}_2\text{O}$
1.49	$\text{BrO}_3^- + 6 \text{H}^+ + 5e = 1/2 \text{Br}_2 + 3 \text{H}_2\text{O}$
1.45	$\text{Ce}^{++++} + e = \text{Ce}^{+++}$
1.45	$\text{ClO}_3^- + 6 \text{H}^+ + 6e = \text{Cl}^- + 3 \text{H}_2\text{O}$
1.42	$\text{BrO}_3^- + 6 \text{H}^+ + 6e = \text{Br}^- + 3 \text{H}_2\text{O}$
1.36	$\text{Au}^{+++} + 3e = \text{Au}$
1.36	$1/2 \text{Cl}_2 + e = \text{Cl}^-$
1.35	$\text{ClO}_4^- + 8 \text{H}^+ + 8e = \text{Cl}^- + 4 \text{H}_2\text{O}$
1.33	$\text{MnO}_2 + 4 \text{H}^+ + 2e = \text{Mn}^{++} + 2 \text{H}_2\text{O}$
1.3	$1/2 \text{Cr}_2\text{O}_7^{--} + 7 \text{H}^+ + 3e = \text{Cr}^{+++} + 7/2 \text{H}_2\text{O}$
1.23	$1/2 \text{O}_2 + 2 \text{H}^+ + 2e = \text{H}_2\text{O}$ (in acid solution)
1.21	$\text{Tl}^{+++} + 2e = \text{Tl}^+$
1.20	$\text{IO}_3^- + 6 \text{H}^+ + 5e = 1/2 \text{I}_2 + 3 \text{H}_2\text{O}$
1.14	Ortho-phenanthroline-ferrous ion (J. Am. Chem. Soc., <b>53</b> , 3908 [1931]) (red in reduced, blue in oxidized form)
1.09	$\text{IO}_3^- + 6 \text{H}^+ + 6e = \text{I}^- + 3 \text{H}_2\text{O}$
1.09	$\text{HSeO}_4^- + 3 \text{H}^+ + 2e = \text{H}_2\text{SeO}_3 + \text{H}_2\text{O}$
1.06	$1/2 \text{Br}_2 + e = \text{Br}^-$
0.94	$\text{NO}_3^- + 4 \text{H}^+ + 3e = \text{NO} + 2 \text{H}_2\text{O}$
0.92	$\text{VO}_3^- + \text{H}_2\text{SO}_4 + 2 \text{H}^+ + e = \text{VOSO}_4 + 2 \text{H}_2\text{O}$
0.90	$\text{Hg}^{++} + e = 1/2 \text{Hg}_2^{++}$
0.86	$\text{Hg}^{++} + 2e = \text{Hg}$
0.84	Diphenylamine sulphonic acid (green in reduced, reddish in oxidized form; satisfactory in presence of tungstates. J. Am. Chem. Soc., <b>53</b> , 2902 [1931])
0.80	$1/2 \text{Hg}_2^{++} + e = \text{Hg}$
0.80	$\text{Ag}^+ + e = \text{Ag}$
0.78	$\text{Fe}^{+++} + e = \text{Fe}^{++}$
0.76	Diphenylbenzidine; green in reduced, violet in oxidized form
0.76	Diphenylamine; colorless in reduced, violet-blue in oxidized form
0.75	$\text{SbO}_4^{--} + 2 \text{H}^+ + 2e = \text{SbO}_3^{--} + \text{H}_2\text{O}$
0.74	$\text{H}_2\text{SeO}_3 + 4 \text{H}^+ + 4e = \text{Se} + 3 \text{H}_2\text{O}$

\* Reprinted from Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, Inc., 1938.

## REDUCTION POTENTIALS \*

Oxidizing Potential Referred to Normal Hydrogen Electrode = 0	Reaction
0.70	$\text{C}_6\text{H}_4\text{O}_2 + 2\text{H}^+ + 2e = \text{C}_6\text{H}_4\text{O}_2\text{H}_2$ (quinhydrone electrode)
0.68	$1/2 \text{O}_2 + \text{H}^+ + e = 1/2 \text{H}_2\text{O}_2$ (reducing action toward stronger oxidants)
0.66	$\text{MnO}_4^- + e = \text{MnO}_4^{--}$
0.59	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e = \text{MnO}_2 + 4\text{OH}^-$
0.57	$\text{AsO}_4^{--} + 2\text{H}^+ + 2e = \text{AsO}_3^{--} + \text{H}_2\text{O}$
0.53	Methylene blue at pH 2.86 [Hygienic Lab. Bul. 171, p. 191 (1928)]
0.53	$1/2 \text{I}_2 + e = \text{I}^-$
0.5	$\text{MoO}_3 + 4\text{H}^+ + e = \text{MoO}^{+++} + 2\text{H}_2\text{O}$
0.49	$\text{Fe}(\text{CN})_6^{--} + e = \text{Fe}(\text{CN})_6^{---}$
0.47	$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e = \text{S} + 3\text{H}_2\text{O}$
*0.4	$\text{VO}_3^- + 6\text{H}^+ + 3e = \text{V}^{++} + 3\text{H}_2\text{O}$
0.4	$\text{VO}^{++} + 2\text{H}^+ + e = \text{V}^{+++} + \text{H}_2\text{O}$
*0.4	$\text{PtCl}_6^{--} + 2e = \text{PtCl}_4^{--} + 2\text{Cl}^-$
0.40	$1/2 \text{O}_2 + \text{H}_2\text{O} + 2e = 2\text{OH}^-$
0.36	$\text{UO}_2\text{SO}_4 + 4\text{H}^+ + \text{SO}_4^{--} + 2e = \text{U}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$
0.34	$\text{Cu}^{++} + 2e = \text{Cu}$
0.333	Decinormal calomel electrode
*0.3	$\text{WO}_3 + 4\text{H}^+ + e = \text{WO}^{+++} + 2\text{H}_2\text{O}$
0.280	Normal calomel electrode
0.23	$\text{AgCl} + e = \text{Ag} + \text{Cl}^-$
0.2	$\text{PtCl}_4^{--} + 2e = \text{Pt} + 4\text{Cl}^-$
0.2	$\text{Bi}^{+++} + 3e = \text{Bi}$
0.17	$\text{S} + 2\text{H}^+ + 2e = \text{H}_2\text{S}$
0.17	$\text{Cu}^{++} + e = \text{Cu}^+$
0.15	$\text{Sn}^{++++} + 2e = \text{Sn}^{++}$
0.14	$\text{SO}_4^{--} + 4\text{H}^+ + 2e = \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$
*0.1	$\text{WO}^{+++} + 2\text{H}^+ + e = \text{W}^{++++} + \text{H}_2\text{O}$
0.04	$\text{TiO}^{++} + 2\text{H}^+ + e = \text{Ti}^{+++} + \text{H}_2\text{O}$
*0.0	$\text{MoO}_3 + 6\text{H}^+ + 3e = \text{Mo}^{+++} + 3\text{H}_2\text{O}$
0.000	$\text{H}^+ + e = 1/2 \text{H}_2$
*-0.1	$1/2 \text{Cb}_2\text{O}_5 + 5\text{H}^+ + 2e = \text{Cb}^{+++} + 5/2 \text{H}_2\text{O}$
-0.12	$\text{Pb}^{++} + 2e = \text{Pb}$
-0.14	$\text{Sn}^{++} + 2e = \text{Sn}$
*-0.2	$\text{CO}_2 + \text{H}^+ + e = 1/2 \text{H}_2\text{C}_2\text{O}_4$
-0.2	$\text{V}^{+++} + e = \text{V}^{++}$
-0.21	$\text{SbO}^+ + 2\text{H}^+ + 3e = \text{Sb} + \text{H}_2\text{O}$
-0.23	$\text{Ni}^{++} + 2e = \text{Ni}$
-0.29	$\text{Co}^{++} + 2e = \text{Co}$
-0.34	$\text{Tl}^+ + e = \text{Tl}$
-0.38	$\text{In}^{+++} + 3e = \text{In}$
-0.40	$\text{Cd}^{++} + 2e = \text{Cd}$
-0.40	$\text{Cr}^{+++} + e = \text{Cr}^{++}$
-0.44	$\text{Fe}^{++} + 2e = \text{Fe}$



TABLE VII—*Continued*

Oxidizing Potential Referred to Normal Hydrogen Electrode = 0	Reaction
-0.5	$\text{Ga}^{+++} + 3e = \text{Ga}$
-0.56	$\text{Cr}^{++} + 2e = \text{Cr}$
-0.76	$\text{Zn}^{++} + 2e = \text{Zn}$
-0.83	$\text{H}_2\text{O} + e = 1/2 \text{H}_2 + \text{OH}^-$
-1.1	$\text{Mn}^{++} + 2e = \text{Mn}$
-1.4	$\text{U}^{++++} + 4e = \text{U}$
-1.69	$\text{Be}^{++} + 2e = \text{Be}$
-1.7	$\text{Al}^{+++} + 3e = \text{Al}$
-2.40	$\text{Mg}^{++} + 2e = \text{Mg}$
-2.71	$\text{Na}^+ + e = \text{Na}$
-2.76	$\text{Ca}^{++} + 2e = \text{Ca}$
-2.90	$\text{Ba}^{++} + 2e = \text{Ba}$
-2.92	$\text{Sr}^{++} + 2e = \text{Sr}$
-2.92	$\text{K}^+ + e = \text{K}$
-2.93	$\text{Rb}^+ + e = \text{Rb}$
-2.96	$\text{Li}^+ + e = \text{Li}$

\* Approximate value or position.

Since the factors  $C_{\text{Cu}^0}$  and  $C_{\text{Zn}^0}$  represent concentrations of metals in the solid form, their values are constant, and we have simply

$$\frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = K \text{ (equilibrium constant)}$$

This means that, when the concentration of zinc ions bears a certain ratio to that of copper ions, the reaction will have come to equilibrium. The equilibrium value can be calculated from considerations of the electrode potentials by applying the Nernst equation.

If a strip of zinc immersed in a solution of a zinc salt is made one electrode and a strip of copper in a cupric salt solution the other electrode, and the two vessels are joined by means of a salt bridge and the electrodes are connected externally through a voltmeter, electric current will flow until the system has come to equilibrium. This will occur when the electrode potential of the zinc equals that of the copper.

From the Nernst equation, for the zinc electrode, we have

$$E_{\text{zinc}} = E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{\text{Zn}^{++}}$$

and for the copper electrode

$$E_{\text{copper}} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{\text{Cu}^{++}}$$

At equilibrium, when the potentials are equal,

$$E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{\text{Zn}^{++}} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{\text{Cu}^{++}}$$

$$E_0 \text{ for zinc} = -0.76 \quad E_0 \text{ for copper} = +0.34$$

$$-0.76 + 0.0295 \log C_{\text{Zn}^{++}} = 0.34 + 0.0295 \log C_{\text{Cu}^{++}}$$

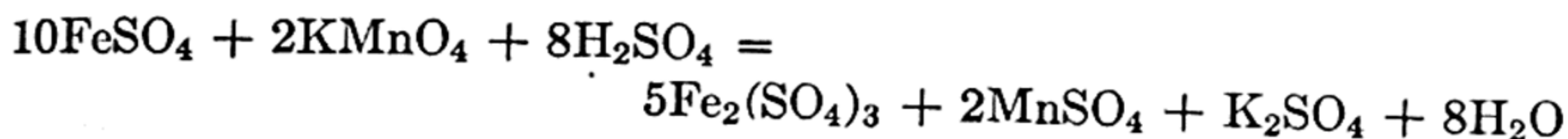
$$0.0295(\log C_{\text{Zn}^{++}} - \log C_{\text{Cu}^{++}}) = 1.10$$

$$\log \frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = 37.3$$

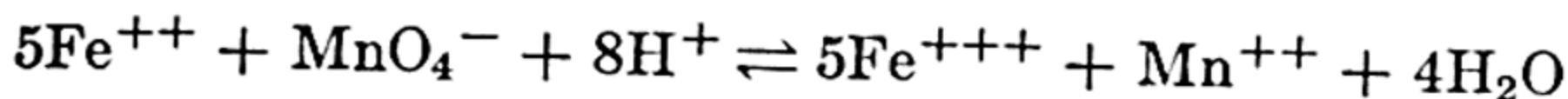
Therefore

$$K = \frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = 1 \times 10^{37.3} = 2 \times 10^{37}$$

**Calculation of the Equilibrium Constant of the Permanganate-Ferrous Reaction.** The oxidation of ferrous salts by potassium permanganate in a strongly acidified solution proceeds according to the reaction



When written ionically it is

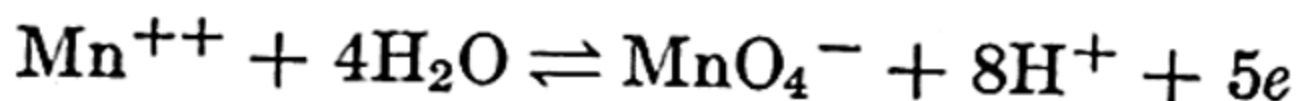


The equilibrium constant of this reaction is therefore expressed in the form

$$\frac{(C_{\text{Fe}^{+++}})^5 \times C_{\text{Mn}^{++}}}{(C_{\text{Fe}^{++}})^5 \times C_{\text{MnO}_4^-} \times (C_{\text{H}^+})^8} = K$$

the  $4\text{H}_2\text{O}$  dropping out from the equilibrium expression since the concentration of  $\text{H}_2\text{O}$  in an aqueous solution is constant.

For the half-cell reaction of a  $\text{MnO}_4^-$ ,  $\text{Mn}^{++}$  electrode the reversible equation is



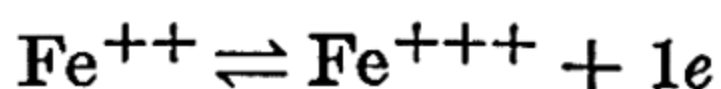
for which the molar electrode potential is given by

$$E = E_0 + \frac{0.059}{5} \log \frac{C_{\text{MnO}_4^-} \times (C_{\text{H}^+})^8}{C_{\text{Mn}^{++}}}$$

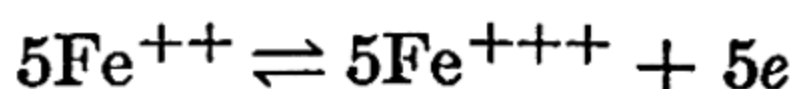
when  $C_{\text{H}^+} = 1$ , the value of  $E_0$  being 1.50 volts.



For the half-cell reaction of a  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$  electrode the reversible equation is



or, to balance the action of the  $\text{MnO}_4^-$ ,  $\text{Mn}^{++}$  electrode, it is



for which the Nernst equation is

$$E = E_0 + \frac{0.0591}{5} \log \frac{(C_{\text{Fe}^{+++}})^5}{(C_{\text{Fe}^{++}})^5}$$

the value of  $E_0$  being 0.78 volt.

Combining the two Nernst equations for a cell which has reached equilibrium,  $E$  for the  $\text{MnO}_4^-$ ,  $\text{Mn}^{++}$  electrode being then equal to  $E$  for the  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$  electrode, we have

$$1.50 + \frac{0.059}{5} \log \frac{C_{\text{MnO}_4^-} \times (C_{\text{H}^+})^8}{C_{\text{Mn}^{++}}} = 0.78 + \frac{0.059}{5} \log \frac{(C_{\text{Fe}^{+++}})^5}{(C_{\text{Fe}^{++}})^5}$$

$$\log \frac{(C_{\text{Fe}^{+++}})^5 \times C_{\text{Mn}^{++}}}{(C_{\text{Fe}^{++}})^5 \times C_{\text{MnO}_4^-} \times (C_{\text{H}^+})^8} = \frac{5(1.50 - 0.78)}{0.059} = 61$$

$$\frac{(C_{\text{Fe}^{+++}})^5 \times C_{\text{Mn}^{++}}}{(C_{\text{Fe}^{++}})^5 \times C_{\text{MnO}_4^-} \times (C_{\text{H}^+})^8} = \log 61 = 1 \times 10^{61}$$

The value of  $K$ , which is expressed by the above ratio of concentrations, is therefore  $1 \times 10^{61}$ , the  $\text{H}^+$ -ion concentration being taken as 1  $M$ .

**Redox Indicators.** A variety of indicators is used for oxidation-reduction titrations. Starch is an excellent indicator for titrations involving iodine; the pink color of the permanganate ion serves as its own indicator; there are external indicators such as potassium ferricyanide for iron titrations. The most interesting indicators, however, are the recently applied internal redox indicators. These are organic substances whose oxidation potential is near that of the ion being titrated. Examples are sodium diphenylamine sulfonate employed in the dichromate method for iron and orthophenanthroline-ferrous complex used in the ceric sulfate titration of iron. Table VII shows the latter to have a potential of 1.14, whereas that of diphenylamine sulfonic acid is 0.84 and diphenylamine itself has a potential of 0.76. At equivalence, the reduced and the oxidized forms of the indicator are present in equal concentrations. The color of the reduced form must, of course, be different from that of the oxidized form.

## QUESTIONS

Balance the following groups of redox equations.

1. (a)  $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{O}_2 + \text{K}_2\text{SO}_4$   
 (b)  $\text{H}_3\text{AsO}_4 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} + \text{S} + \text{H}_3\text{AsO}_3$   
 (c)  $\text{Na}_2\text{O}_2 + \text{CrCl}_3 + \text{NaOH} \rightarrow \text{Na}_2\text{CrO}_4 + \text{NaCl} + \text{H}_2\text{O}$
2. (a)  $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{CO}_2 + \text{K}_2\text{SO}_4$   
 (b)  $\text{H}_2\text{O}_2 + \text{FeCl}_2 + \text{HCl} \rightarrow \text{FeCl}_3 + \text{H}_2\text{O}$   
 (c)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} + \text{SnCl}_2 \rightarrow \text{CrCl}_3 + \text{H}_2\text{O} + \text{SnCl}_4 + \text{KCl}$
3. (a)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} + \text{H}_2\text{S} \rightarrow \text{CrCl}_3 + \text{H}_2\text{O} + \text{S} + \text{KCl}$   
 (b)  $\text{Cl}_2 + \text{KI} \rightarrow \text{I}_2 + \text{KCl}$   
 (c)  $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{KI} \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{I}_2 + \text{K}_2\text{SO}_4$
4. (a)  $\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$   
 (b)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} + \text{KI} \rightarrow \text{CrCl}_3 + \text{H}_2\text{O} + \text{I}_2 + \text{KCl}$   
 (c)  $\text{NaOCl} + \text{HI} \rightarrow \text{I}_2 + \text{H}_2\text{O} + \text{NaCl}$
5. (a)  $\text{KMnO}_4 + \text{H}_2\text{O} + \text{MnSO}_4 \rightarrow \text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$   
 (b)  $\text{HClO}_3 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_4 + \text{HCl}$   
 (c)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{CO}_2 + \text{K}_2\text{SO}_4$
6. (a)  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} + \text{MnSO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{MnO}_2 + \text{H}_2\text{SO}_4$   
 (b)  $\text{HNO}_3 (\text{dil}) + \text{Bi}_2\text{S}_3 \rightarrow \text{NO} + \text{H}_2\text{O} + \text{S} + \text{Bi}(\text{NO}_3)_3$   
 (c)  $\text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{CO}_2$
7. (a)  $\text{KMnO}_4 + \text{HCl} + \text{H}_2\text{S} \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{S} + \text{KCl}$   
 (b)  $\text{KIO}_3 + \text{I}_2 + \text{HCl} \rightarrow \text{ICl} + \text{H}_2\text{O} + \text{KCl}$   
 (c)  $\text{HNO}_3 + \text{H}_2\text{S} \rightarrow \text{NO} + \text{H}_2\text{O} + \text{S}$
8. (a)  $\text{I}_2 + \text{HAsO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + \text{HI}$   
 (b)  $\text{HNO}_2 + \text{H}_2\text{S} \rightarrow \text{S} + \text{NO} + \text{H}_2\text{O}$   
 (c)  $\text{KMnO}_4 + \text{H}_2\text{O} + \text{Na}_2\text{SnO}_2 \rightarrow \text{MnO}_2 + \text{KOH} + \text{Na}_2\text{SnO}_3$
9. (a)  $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{HNO}_2 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{HNO}_3 + \text{K}_2\text{SO}_4$   
 (b)  $\text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{NaI} \rightarrow \text{MnSO}_4 + \text{I}_2 + \text{NaHSO}_4 + \text{H}_2\text{O}$   
 (c)  $\text{HNO}_3 (\text{conc}) + \text{As}_2\text{S}_5 \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4$
10. (a)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_3 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{K}_2\text{SO}_4$   
 (b)  $\text{MnO}_2 + \text{HCl} \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2$   
 (c)  $\text{Sb}_2\text{S}_5 + \text{HCl} (\text{conc}) \rightarrow \text{SbCl}_3 + \text{S} + \text{H}_2\text{S}$

## REPRESENTATIVE OXIDATION-REDUCTION PROCEDURES

An oxidation-reduction reaction must run practically to completion if it is to be used as the basis of a quantitative volumetric method of analysis. Not all oxidation-reduction reactions fulfill this requirement, and it is essential to select the proper combination of oxidizing and reducing agents, one of which constitutes the substance being analyzed, the other being the standard solution with which the sample is titrated. In practice it is often desirable to have at hand two standard solutions, the one an oxidizing agent and the other a reducing agent, so that, if an excess of one reagent is deliberately or accidentally added, this excess may be determined by means of the other reagent.



The selection of proper combinations is further restricted by the additional requirements of the standard solution. A solution, it must be remembered, in order to be used as the titrating medium (1) must react practically quantitatively with the material being titrated, (2) must not change strength, (3) must be standardized by a reaction which runs practically to completion, and (4) must be used in connection with an indicator whose color change coincides very closely with the stoichiometric point of the reaction. These requirements place restrictions on the possible number of standard solutions but, in spite of this, redox methods constitute by far the most important class of volumetric methods.

**Classification of Oxidation-Reduction Methods.** It is convenient to classify volumetric oxidation-reduction methods on the basis of the standard solution used in the fundamental reaction. Among oxidizing agents, potassium dichromate, potassium permanganate and iodine are found to be the most satisfactory as standard solutions. In addition, potassium iodate and potassium bromate are frequently used. Ceric sulfate is now coming into use as a standard oxidizing solution. In connection with these oxidizing agents, ferrous salts, oxalic acid, sodium thiosulfate, sodium arsenite and potassium iodide may be employed; these are strong reducing agents and, with the exception of potassium iodide, are generally used in the form of standard solutions. Suitable pairs of these reagents are:

- Potassium dichromate with ferrous salts.
- Potassium permanganate with ferrous salts.
- Potassium permanganate with oxalic acid.
- Ceric sulfate with ferrous salts.
- Iodine with sodium arsenate.
- Iodine with sodium thiosulfate.
- Potassium iodide with oxidizing agents.

For the purpose of study and laboratory experimentation, these combinations are considered under the following types of methods:

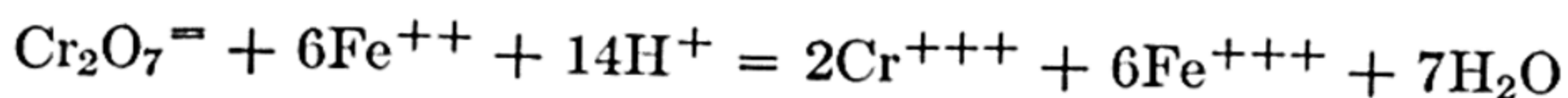
- A. Dichromate methods.
- B. Permanganate methods.
- C. Ceric sulfate methods.
- D. Iodine methods.

Use is made of standard solutions of potassium dichromate and ferrous sulfate in the determination of iron in the laboratory procedure described first. The determination of iron, involving the use of standard potassium permanganate and ferrous sulfate solutions, and the determination of

calcium, involving standard permanganate and oxalic acid solutions, are described under permanganate methods. The use of standard ceric sulfate solution is outlined. Methods which involve reactions of iodine or its compounds are discussed and procedures based on these reactions are taken up under that heading.

### A. DICHROMATE METHODS

Volumetric oxidation-reduction methods which involve the dichromate ion are comparatively few in number. The reaction between ferrous ions and the dichromate ion is the most important one, and it serves as a basis for the determination of both iron and chromium, as well as, indirectly, for a number of other substances. The fundamental reaction is



A standard solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  may be used to determine the amount of iron in a given sample and, on the other hand, chromium in ores and salts may be converted into the dichromate ion and titrated with a standard solution of a ferrous salt.

### DICHROMATE DETERMINATION OF IRON

In the dichromate method for the determination of iron, the iron is first reduced to the ferrous state by stannous chloride. The excess of stannous chloride is then oxidized and removed by mercuric chloride. An acid mixture, containing sulfuric and phosphoric acids, is added and the titration is carried out with standard potassium dichromate solution, using sodium diphenylamine sulfonate as indicator. Standard ferrous salt solution is prepared in case it is needed for back-titration.

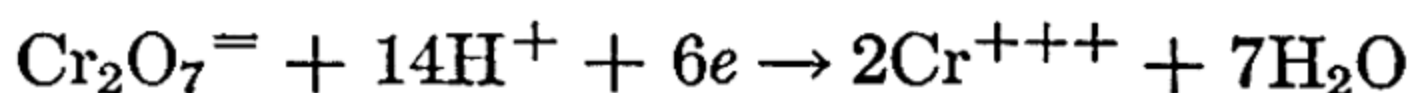
The potassium dichromate solution may be made from primary standard  $\text{K}_2\text{Cr}_2\text{O}_7$  or else standardized with weighed amounts of iron wire of known purity, but the strength of the ferrous sulfate solution is obtained by comparison with the dichromate solution.

The acid mixture reduces the pH of the iron solution to a definitely acid region. This is necessary in order to have the oxidation-reduction potential of the ferrous-ferric system near that of the potential of the diphenylamine sulfonate indicator. The phosphoric acid, by combining with ferric ions produced in the titration to form a colorless acid phosphate complex, eliminates the disturbing color effect of the yellow ferric chloride. Furthermore, the removal of ferric ions keeps the ferrous-ferric concentration ratio high, and prevents the oxidation of the indicator until the ferrous-ion concentration becomes negligible.

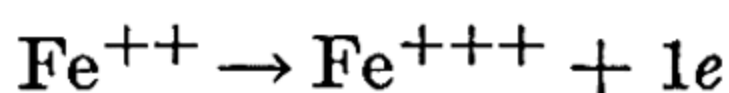


*Preparation and Standardization of Approximately 0.1 N Solutions  
of Potassium Dichromate and Ferrous Sulfate*

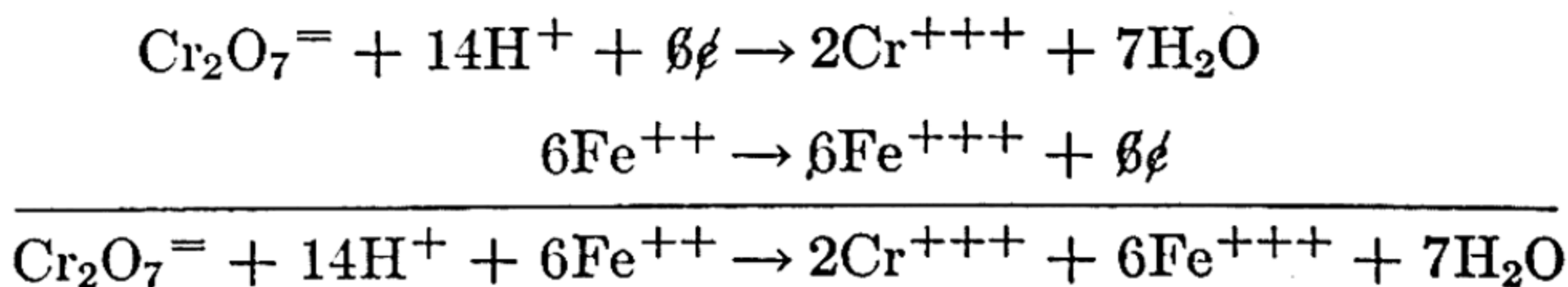
In the reaction between the dichromate ion and ferrous ions in the presence of acid, the chromium in the  $\text{Cr}_2\text{O}_7^{=}$  ion becomes reduced to  $\text{Cr}^{+++}$  ions, and the  $\text{Fe}^{++}$  ions are oxidized to the ferric,  $\text{Fe}^{+++}$ , state. Each chromium atom in the dichromate ion is reduced from a valence of +6 to a valence of +3. Hence, since there are two atoms of chromium involved in one  $\text{Cr}_2\text{O}_7^{=}$  ion, the total valence change, for this ion, is 6. This means an acceptance of three electrons for each chromium atom or a total of six for both atoms, as shown by the electron or half-cell equation



The iron atom loses an electron in being raised from a valence of +2 to a valence of 3, in accordance with the equation

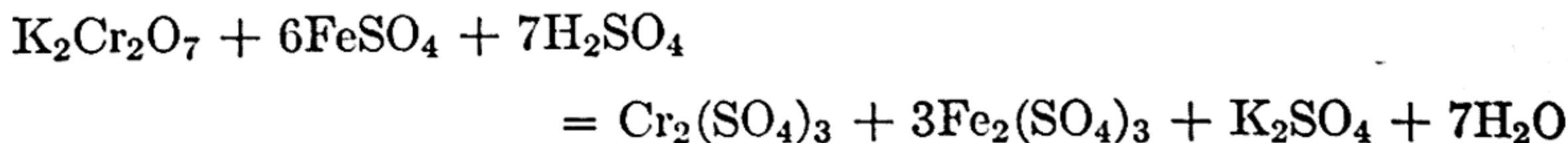


Hence, to balance the equation for the reaction between  $\text{Cr}_2\text{O}_7^{=}$ ,  $\text{Fe}^{++}$  and  $\text{H}^+$  ions, we have



This ionic reaction is the basis for the standardization of the dichromate solution as well as for the determination of iron.

For the preparation of the dichromate solution, potassium dichromate is used. From the reaction in molecular form



it is seen that one mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  reacts with six moles of ferrous sulfate. A normal solution of an oxidizing agent is one that contains a gram-equivalent weight per liter. The gram-equivalent weight for an oxidizing agent is defined as that weight which corresponds to one unit change in valence or the gain of one electron. For  $\text{K}_2\text{Cr}_2\text{O}_7$ , since the total change of valence is 6, in order to make a normal solution there is required one-sixth of the molecular weight in grams per liter. The molecular weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 294.21. A normal solution therefore

calls for 49.03 grams, and an exactly 0.1 *N* solution for 4.903 grams of the pure salt per liter.

For a 0.1 *N* solution of the ferrous salt, one-tenth of the molecular weight should be taken, since each iron ion in being oxidized from the ferrous to the ferric condition undergoes a valence change of 1. Crystallized ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , or ferrous ammonium sulfate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , may be used, approximately 28 grams of the former or 40 grams of the latter for a liter of the solution of approximate 0.1 *N* strength.

**Preparation of Solutions.** Procure 5 grams of  $\text{K}_2\text{Cr}_2\text{O}_7$  and 28 grams of hydrated ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  or, if this salt is not to be had, 40 grams of ferrous ammonium sulfate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Mohr's Salt).

Pulverize the 5 grams of potassium dichromate and dissolve in about 200 ml. of distilled water, warming if necessary. Transfer the solution to a liter measuring flask and dilute to the mark. This solution is approximately 0.1 *N*. It should be noted here that potassium dichromate can be procured of sufficiently high purity so that an accurately weighed amount (4.903 grams) will give a standard solution of the desired normality directly.

Dissolve the ferrous salt in distilled water, add 5 ml. of concentrated  $\text{H}_2\text{SO}_4$  and transfer to a liter flask, making up the volume to 1 liter. Keep the solution in a liter bottle. This solution is likewise approximately 0.1 *N*.

Stannous chloride and mercuric chloride reagents are supplied in the laboratory. The former is prepared by dissolving 50 grams of stannous chloride in 100 ml. of concentrated hydrochloric acid and diluting to 1 liter with distilled water. A few pieces of metallic tin added to the reagent prevents oxidation to the stannic state. The mercuric chloride is a saturated solution.

The acid mixture is made by slowly adding 120 ml. of concentrated sulfuric acid and 35 ml. of concentrated (85 per cent) phosphoric acid to 850 ml. of distilled water. Be sure the solution is cool before using.

**Comparison of Solutions.** Clean and rinse two burets; fill one with the ferrous salt solution and the other with the potassium dichromate solution. Into a 500-ml. Erlenmeyer flask run about 30 ml. of the ferrous sulfate solution, acidify it with 200 ml. of acid mixture. Add 6 to 8 drops of diphenylamine sulfonate indicator. Now, slowly and with constant swirling of the flask, run the dichromate solution into the ferrous salt solution. When the color changes from green to bluish gray, add the dichromate solution drop by drop. The end point is a purple color which persists for at least one minute. If the end point should be passed,

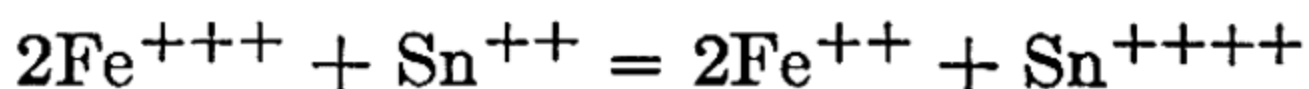


add 1 or 2 ml. of the ferrous salt solution and again approach the end point, by careful addition of dichromate solution.

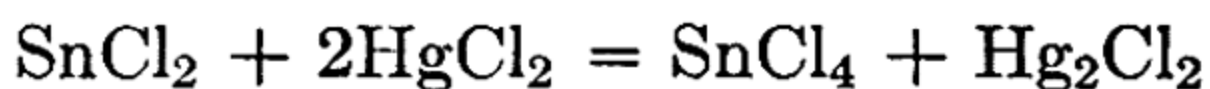
Refill both burets and make another comparison, using approximately the same volumes as before.

From the volumes of the two solutions used to complete the reaction, calculate the number of milliliters of ferrous salt solution required to react with 1 ml. of dichromate solution.

**Standardization of Dichromate by Iron Wire.** Unless the potassium dichromate used is of sufficient purity so that the solution, as made up under the procedure described above, may be regarded as of the exact desired strength, it is necessary to standardize the dichromate solution. The best primary standard is electrolytic iron, but iron wire of high and known purity may serve the purpose here. The wire is dissolved in hydrochloric acid and, since the oxygen of the air may oxidize some of the dissolved iron, it is necessary to make certain that all the iron is in the ferrous state. The solution is reduced with stannous chloride, according to the reaction



An excess of stannous chloride is unavoidable; but this excess must be removed because, being a reducing reagent, it will react with the dichromate solution and introduce a serious error. The excess is removed by mercuric chloride, which reacts according to the equation



Procure from the instructor about 1 gram of iron wire. Examine it carefully for rust and, if rust is present, remove it by rubbing with sandpaper. Weigh out three separate portions of iron wire of about 0.2000 gram each. Ascertain the purity of the iron wire.

Into each of three 500-ml. Erlenmeyer flasks place 10 ml. of concentrated HCl and 10 ml. of distilled water, cover with watch glasses and bring just to boiling. Remove the flasks from the flame and into each flask drop the portion of the iron wire as weighed out. Cover with watch glasses and boil until the wire is dissolved. Wash down the sides of the flasks and the watch glasses with distilled water from the wash bottle.

In continuing the procedure beyond this point, carry each individual solution of iron through to the end of the titration before starting to reduce the next one.

Add stannous chloride ( $\text{SnCl}_2$ ) solution dropwise to the first solution, which has been reheated to boiling, until it becomes colorless or slightly

green. Only a few drops should be necessary. Then add one drop in excess. Thoroughly cool under the water tap and add 10 ml. of saturated  $\text{HgCl}_2$  solution. If sufficient  $\text{SnCl}_2$  solution was used in the reduction of the standard iron, a silky white precipitate of mercurous chloride will be formed. If this precipitate is not obtained, the reduction of the iron was not complete, and the solution must be discarded. Furthermore, if too much stannous chloride was added, a black precipitate of free mercury will be formed; in this case the solution must likewise be discarded. Allow to stand for three minutes. Dilute with 200 ml. of acid mixture. Add 6 to 8 drops of the indicator and titrate slowly with the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution until the green color changes through a gray to the purple end point. The purple color should persist for at least one minute.

Reduce and titrate the second dissolved standard as just described. Do likewise with the third. From the net volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  used, calculate the iron titer of the dichromate solution and from this the normality of the solution. Also, from the comparison data calculate the normality of the ferrous solution. Repeat the entire standardization if the results do not check within 3 parts per 1000.

#### *Determination of Iron in Iron Ore*

**Procedure.** Weigh accurately three portions of the sample of iron ore of about 0.5 gram which has been dried and, if organic material was present, ignited, into three numbered 500-ml. Erlenmeyer flasks. Add 20 ml. of distilled water, cover the flasks with watch glasses and heat to boiling. Add 25 ml. of hot concentrated  $\text{HCl}$  and continue to heat. This treatment should dissolve the ore sample in 15 to 20 minutes. From time to time replace the acid lost by evaporation. When the sample is dissolved, there may be a residue of white siliceous material present, but no dark iron oxide particles. If the sample does not dissolve in half an hour, the addition of 1 ml. of stannous chloride solution may hasten the reaction. When complete solution is obtained wash down the sides of the flasks and the watch glasses with distilled water.

From this point on, as in the standardization, carry each individual solution of iron through to the end of the titration before starting the reduction of the next sample.

To the first iron solution, reheated to boiling, add stannous chloride solution dropwise until the solution becomes colorless or pale green. Considerably more stannous chloride will be used here than was used in the standardization. Add one drop in excess. Cool under the water tap. When thoroughly cold add 10 ml. of saturated  $\text{HgCl}_2$  solution.



If sufficient stannous chloride solution was used to reduce the iron completely to the ferrous state, a silky white precipitate of mercurous chloride will be formed. If no precipitate forms, or if a dark precipitate of free mercury is obtained, the determination must be discarded.

Allow the solution to stand for three minutes. Dilute with 200 ml. of acid mixture and add 6 to 8 drops of indicator. Titrate slowly with the  $K_2Cr_2O_7$  solution. As the end point is approached the green color changes to gray. Now add the dichromate solution dropwise until a purple color lasting for at least one minute is obtained.

Reduce and titrate the second sample of iron ore in a similar manner. Repeat with the third sample.

From the data obtained calculate the percentage of iron in the sample.

### QUESTIONS

1. Define a normal oxidizing solution and a normal reducing solution. Show how the amount of  $K_2Cr_2O_7$  and  $FeSO_4 \cdot 7H_2O$  required for 1 liter of solutions of 0.1 normality is determined.
2. Where, in qualitative analysis, was the stannous chloride-mercuric chloride reaction used?
3. If too much stannous chloride is used, and the subsequent addition of mercuric chloride results in a deposit of metallic mercury, why cannot the solution be titrated with potassium dichromate?
4. What is the qualitative test for ferrous ion? For ferric ion? What is Prussian blue? Turnbull's blue?
5. Give the equation for the reaction between chromic ions and  $Na_2O_2$ . On the basis of this preliminary oxidation devise a method for the volumetric determination of a chromic salt.
6. Suppose you had on hand a standard solution of  $KMnO_4$  and supplies of ferrous sulfate; how would you standardize a  $K_2Cr_2O_7$  solution?

### PROBLEM SET 6

#### DICHROMATE CALCULATIONS

1. Find (a) the Fe titer, (b) FeO titer, (c)  $Fe_2O_3$  titer of a 0.1200 N  $K_2Cr_2O_7$  solution.  

Ans. (a) 0.006702  
(b) 0.008622  
(c) 0.009582
2. What weights of  $K_2Cr_2O_7$  are required to prepare liter solutions of the following normalities: (a) 0.0500; (b) 0.1100; (c) 0.5000? Find the corresponding Fe titers.
3. A reducing solution was prepared by dissolving 45 grams of Mohr's salt in sufficient water to make a liter of solution. How much  $K_2Cr_2O_7$  should be used to prepare 750 ml. of solution, equivalent to the reducing solution? Ans. 5.640 grams
4. A student standardized a  $K_2Cr_2O_7$  solution against iron wire which was 99.80 per cent pure and found that a 0.2250-gram sample of wire required 38.46 ml. of  $K_2Cr_2O_7$  solution. Find the normality of the  $K_2Cr_2O_7$  solution.

5. The following data were obtained by a student during an iron determination.

Comparison of solutions

$$33.89 \text{ ml. K}_2\text{Cr}_2\text{O}_7 \approx 30.65 \text{ ml. FeSO}_4$$

Standardization

$$\begin{aligned} \text{Weight of iron wire (99.8 per cent pure)} &= 0.2055 \text{ gram} \\ \text{Volume of K}_2\text{Cr}_2\text{O}_7 \text{ used} &= 38.12 \text{ ml.} \\ \text{Volume of FeSO}_4 \text{ used} &= 2.63 \text{ ml.} \end{aligned}$$

Analysis

$$\begin{aligned} \text{Weight of sample} &= 0.5023 \text{ gram} \\ \text{Volume of K}_2\text{Cr}_2\text{O}_7 \text{ used} &= 34.63 \text{ ml.} \\ \text{Volume of FeSO}_4 \text{ used} &= 1.59 \text{ ml.} \end{aligned}$$

Find the percentage of iron in the sample.

*Ans.* 38.12 per cent.

6. How much iron ore should be taken so that each milliliter of a 0.1050  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution will represent 1 per cent of Fe in the sample?

7. An ignited residue of a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  obtained in a limestone analysis weighed 0.3010 gram. This was fused with  $\text{KHSO}_4$  and dissolved in sulfuric acid, reduced, and the iron titrated with 32.72 ml. of 0.1025  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Find the weights of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the sample.

*Ans.* 0.2678 gram  $\text{Fe}_2\text{O}_3$ ; 0.0332 gram  $\text{Al}_2\text{O}_3$

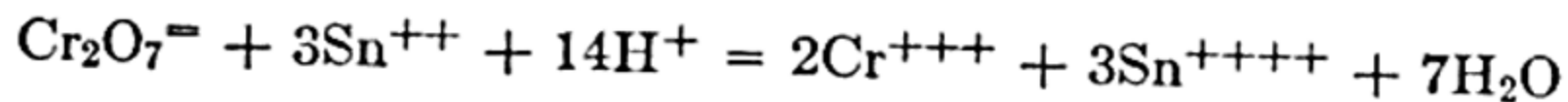
8. What proportions of 0.1096  $N$  and 0.0960  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  solutions should be mixed to give a 0.1000  $N$  solution?

9. How much water must be added to 925 ml. of a 0.1015  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution in order to make a solution which is 0.1000  $N$ ?

*Ans.* 14 ml.

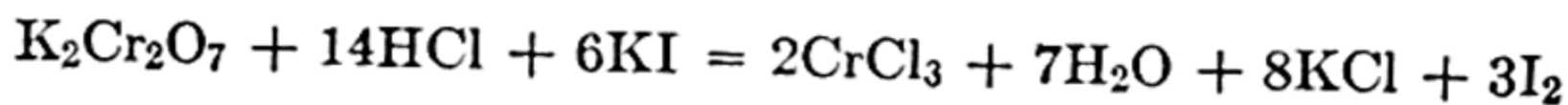
10. In the analysis of a chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) the sample was fused and oxidized with sodium peroxide and the melt acidified, thus converting the chromium into  $\text{Na}_2\text{Cr}_2\text{O}_7$ . What is the percentage of chromium in a 0.2500-gram sample if 42.19 ml. of 0.1025  $N$   $\text{FeSO}_4$  were added to the material treated as above and 2.34 ml. of 0.0998  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  were required to titrate the excess  $\text{FeSO}_4$ ?

11. Calculate the volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution having a normality of 0.09840 that will react with 0.5213 gram of pure  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , basing the method on the following equation:

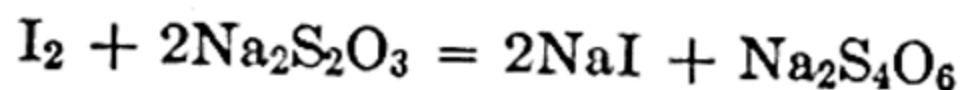


*Ans.* 46.96 ml.

12. In standardizing a  $\text{Na}_2\text{S}_2\text{O}_3$  solution, by titrating the  $\text{I}_2$  liberated from KI by the action of a standardized solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , in accordance with the following reactions:



and



the following data were secured:

$$\begin{aligned} \text{volume of K}_2\text{Cr}_2\text{O}_7 \text{ used} &= 35.23 \text{ ml.} \\ \text{normality of K}_2\text{Cr}_2\text{O}_7 &= 0.1025 \text{ N} \\ \text{volume of Na}_2\text{S}_2\text{O}_3 \text{ used} &= 30.55 \text{ ml.} \end{aligned}$$

Calculate the normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution.



13. Calculate the percentage of iron in a limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) sample, the analysis of which gave the following data:

weight of sample	= 0.4500 gram	normality of $\text{K}_2\text{Cr}_2\text{O}_7$	= 0.1050
volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used	= 38.64 ml.	" "	$\text{FeSO}_4$ = 0.1250
volume of $\text{FeSO}_4$ used	= 3.62 ml.		Ans. 44.73 per cent

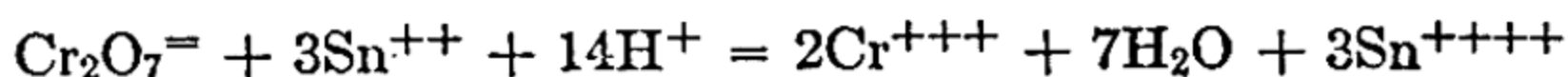
14. Calculate the normality of a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution from the following data:

25.82 ml. of $\text{K}_2\text{Cr}_2\text{O}_7$	$\approx$	31.25 ml. of $\text{FeSO}_4$
33.26 ml. of $\text{KMnO}_4$	$\approx$	33.80 ml. of $\text{FeSO}_4$
1 ml. of $\text{KMnO}_4$	=	0.005855 gram Fe

15. What weight of iron ore sample should be taken for analysis if the percentage of iron in the sample is approximately 40 per cent and not over 35 ml. of a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, whose normality is 0.1000 *N*, are to be used? Ans. 0.4888 gram

16. A certain solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 0.6025 *N*. What volume of water must be added to 500 ml. of this solution so that each milliliter of the solution will represent 2 per cent of Fe when a 0.5000-gram sample of iron ore is taken for analysis?

17. What volume of a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution having an Fe titer of 0.005674 will be required to react with 0.3125 gram of pure  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ? The reaction is



Ans. 27.30 ml.

18. Calculate the percentage of chromium in a 0.6223-gram sample of chromium ore if, after conversion of the ore to the  $\text{Cr}_2\text{O}_7^{=+}$  form, the titration required 33.65 ml. of a 0.2000 *N*  $\text{FeSO}_4$  solution.

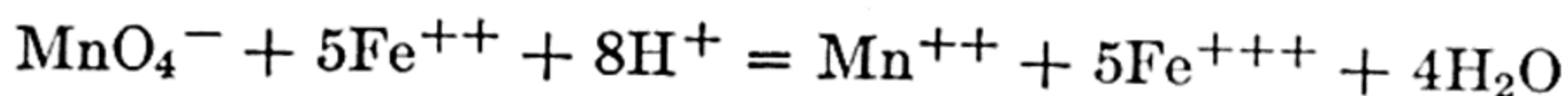
19. What weight of pure  $\text{K}_2\text{Cr}_2\text{O}_7$  should be taken in order to make 500 ml. of a solution which should have an Fe titer of 0.005000? What weight of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (assumed pure) is required to make a liter of a solution of the same strength? Ans. 2.197 grams; 35.13 grams

20. A student reported 52.62 and 52.60 per cent iron, respectively. What was the precision of his work? If the true value was 52.50 per cent iron what was the accuracy of his average result?

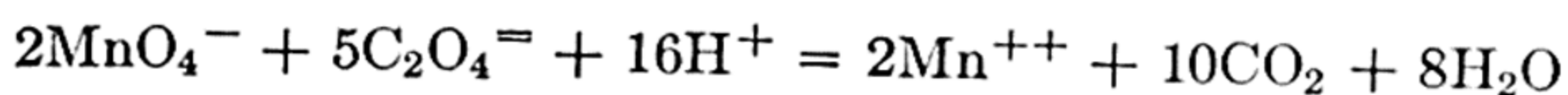
## B. PERMANGANATE METHODS

Methods of analysis based upon the reactions of the permanganate ion are among the most important of the volumetric processes. The permanganate ion is one of the strongest oxidizing agents, and this, together with the fact that a slight excess of permanganate ion gives to a solution a decidedly pink color, thus acting as its own indicator, make standard solutions of permanganate among the most valuable and widely employed oxidizing agents in volumetric analysis. The permanganate ion reacts quantitatively with a large number of reducing substances in an acid solution and with certain other substances in a neutral or basic solution. For these reasons potassium permanganate, the salt usually employed, has a wide application for the determination of a large number of substances under a variety of experimental conditions.

**Fundamental Reactions of the Permanganate Ion.** In an acid medium two reactions in particular are of fundamental importance, not only because they form the basis of a large number of excellent methods of analysis but also because they are employed in the usual methods of standardization of permanganate solutions. With ferrous salts the following reaction takes place:

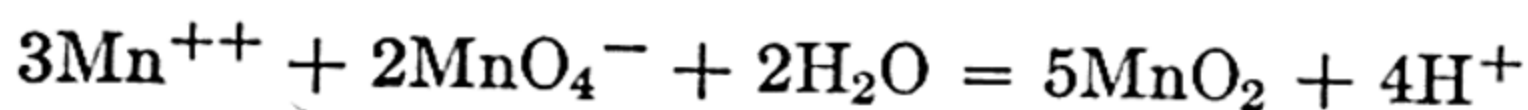


and with oxalic acid:



By the use of a standard solution of potassium permanganate in an acid solution in conjunction with standard solutions of either ferrous sulfate or oxalic acid, a great many determinations can be carried out, and modifications can be introduced into the experimental details to cover the analysis of a large number of elements and their compounds. In the first place, standard permanganate can be titrated directly into solutions of reducing substances, whereby the material in the reduced form is oxidized. Also, an excess of ferrous salt or oxalic acid may be added to the sample to bring about a preliminary reduction of the material and the unused excess of reagent determined by titration with standard permanganate solution. Furthermore, insoluble oxalates can be precipitated and separated from interfering substances and these precipitates dissolved in  $\text{H}_2\text{SO}_4$  and the liberated oxalate ion then titrated with standard  $\text{KMnO}_4$ .

The behavior of potassium permanganate in neutral and basic solutions is different from that in an acid solution. Under these conditions the reduction of the  $\text{MnO}_4^-$  ion is not to the divalent  $\text{Mn}^{++}$  ion but to tetravalent manganese, the manganese being precipitated as hydrated  $\text{MnO}_2$ . As an example, manganous ions,  $\text{Mn}^{++}$ , can be oxidized to  $\text{MnO}_2$  by the permanganate ion:



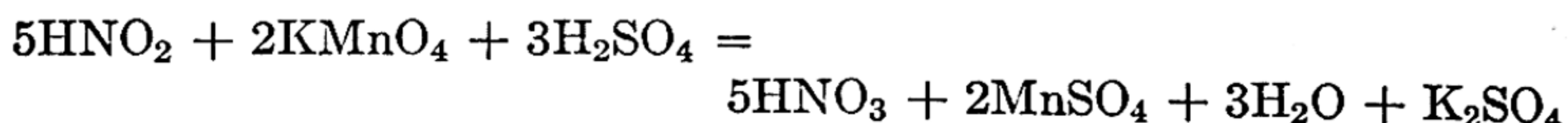
The manganese in the  $\text{MnO}_4^-$  is here reduced from an apparent valence of +7 to a valence of +4. This fundamental reaction is the basis of a method for the determination of manganese in steel.

**Uses of Permanganate Solutions.** As indicated, standard potassium permanganate in an acidic solution may be used (1) to titrate, directly, many substances which are present in the reduced state, (2) to titrate unused excess of a reducing agent, (3) to titrate reducing agents liberated by suitable reactions from the material being analyzed and (4) to titrate certain substances in a neutral or basic solution.



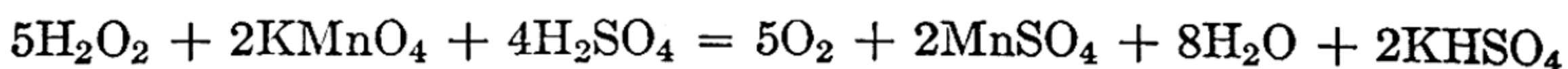
1. DETERMINATIONS BY DIRECT OXIDATION. By method 1 we can determine a great many elements and their compounds, provided the substance to be titrated is present in the lower state of oxidation. An example of this type of procedure is the volumetric determination of iron, the procedure for which is given below as a laboratory exercise. Oxalic acid and soluble oxalates may be determined by a similar titration, based on the reaction already given.

Nitrites may be quantitatively oxidized according to the reaction



by titration with standard permanganate.

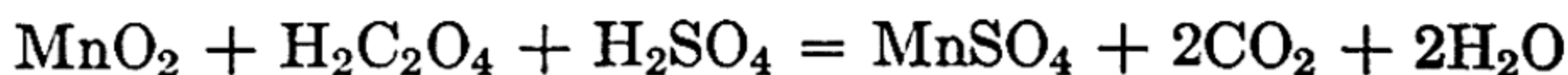
Hydrogen peroxide reacts in the following manner:



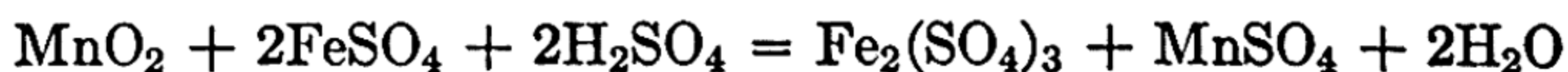
the peroxide acting here as a reducing agent and being oxidized to free oxygen.

2. TITRATION OF EXCESS REDUCING AGENT. In method 2 the details of analysis are so arranged that the material being analyzed is quantitatively reduced by adding either a weighed amount of reducing agent known to be in excess or, alternatively, by adding a measured volume of standardized reducing agent such as a ferrous salt or an oxalic acid solution known to be in excess and then titrating the unused excess with standard permanganate solution. A number of important determinations, such as the following, are based on this mode of procedure.

The determination of the purity of pyrolusite, an impure ore of manganese dioxide, is an example of this type. To a weighed amount of the sample an excess of  $\text{H}_2\text{C}_2\text{O}_4$  is added, the  $\text{MnO}_2$  being reduced to the manganous form:



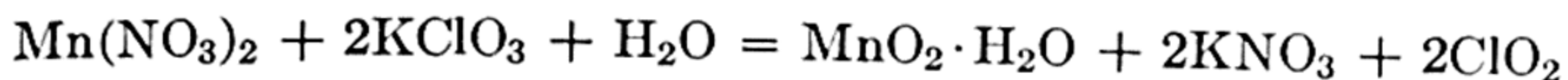
In place of oxalic acid, a ferrous salt may be used as reducer, the reaction in this case being



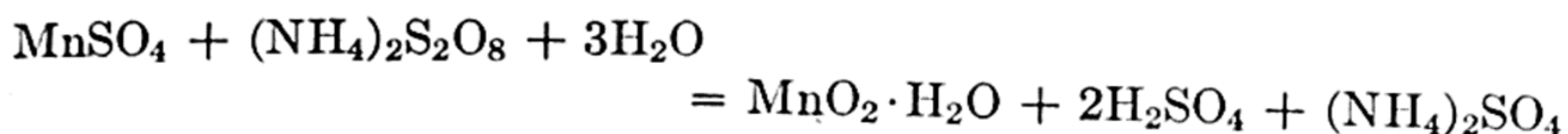
The excess of reducing agent may then be determined by titration with standard permanganate and from this the purity of the sample may be determined.

By modifications of the above method, manganese in steel can be determined. Two such metallurgical methods may be mentioned. In one, known as the Williams method, the steel is dissolved, the manganese oxidized to  $\text{MnO}_2$  by means of potassium chlorate, the  $\text{MnO}_2$  again

reduced by an excess of standard reducing agent and the excess titrated, as in other indirect methods, with potassium permanganate. The preliminary oxidation of the manganese is indicated by the reaction

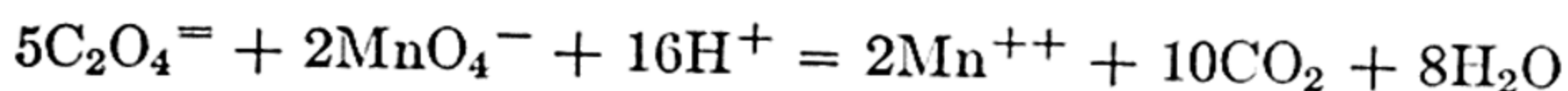


In the other modification, the persulfate method, the preliminary oxidation of the manganese is accomplished by means of ammonium persulfate:



the subsequent treatment being the same in principle as the other method. For details of these methods, a text on metallurgical analysis, such as Lundell, Hoffman and Bright *Chemical Analysis of Iron and Steel*, should be consulted.

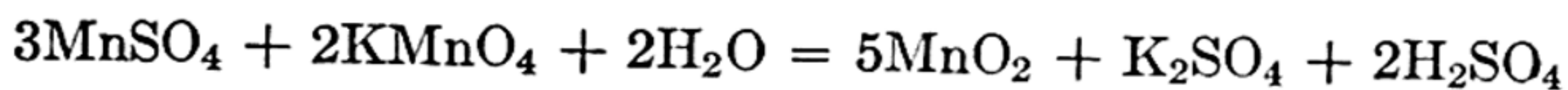
3. LIBERATION OF REDUCING AGENT. Among the methods based on the formation of reducing agent, which in turn is determined by titration with permanganate, may be mentioned those in which an oxalate is precipitated. The oxalates of many metals are relatively insoluble in water but readily dissolve in dilute sulfuric acid to liberate the oxalate ion. The qualitative test for calcium and conversely that for the oxalate ion will call to mind the basis of the method upon which determinations of this kind rest. The determination of calcium, gravimetrically, by precipitation as  $\text{CaC}_2\text{O}_4$  (see page 201) may be modified by redissolving the  $\text{CaC}_2\text{O}_4$  in  $\text{H}_2\text{SO}_4$  and titrating the liberated oxalic acid with  $\text{KMnO}_4$ , thus involving the fundamental reaction



This determination is described in the procedure given later and is representative of analyses of this type.

In addition to calcium, the ions of barium, strontium, copper, lead, zinc and mercurous mercury can be precipitated as oxalates and subsequently determined in a similar manner.

4. USE OF PERMANGANATE IN NEUTRAL OR BASIC SOLUTIONS. As already indicated, permanganate is reduced only to the tetravalent state, when acted upon by certain reducing agents in a basic or neutral solution. In the example cited, the reaction



is peculiar in the fact that one compound of manganese,  $\text{KMnO}_4$ , is used to oxidize another manganese compound,  $\text{MnSO}_4$ , resulting in a third manganese compound,  $\text{MnO}_2$ . The valence change of the manganese



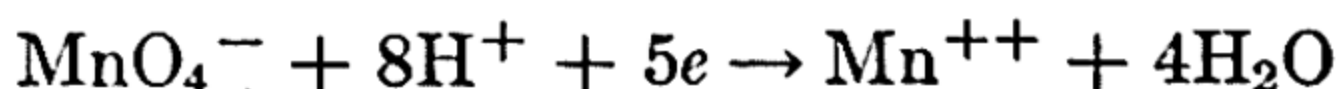
in the  $\text{MnO}_4^-$  ion is from  $+7$  to  $+4$ , a change of 3 valence units, whereas the manganous ion,  $\text{Mn}^{++}$ , is oxidized from  $+2$  to  $+4$ . Potassium permanganate acting thus as an oxidizing agent in a neutral solution is capable of accepting only three electrons instead of five. In conformity with the definition of a normal oxidizing solution, since there is a change of three valence units (a gain of three electrons), the amount of potassium permanganate required for a normal solution to be used under these conditions is therefore one-third of the gram-molecular weight. In acidified solutions, however, only one-fifth of the molecular weight in grams is required for a normal solution.

### PERMANGANATE DETERMINATION OF IRON

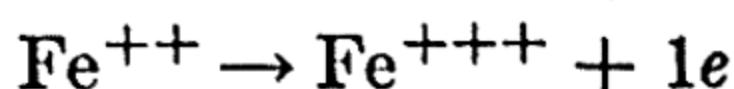
The determination of iron by the permanganate method is based on the quantitative oxidation of the ferrous ion by potassium permanganate. The process involves a preliminary reduction of the iron to the ferrous condition, the preparation and standardization of approximately one-tenth normal solutions of potassium permanganate and of ferrous sulfate and the titration of the reduced iron sample with the standard permanganate solution, in a solution acid with sulfuric acid. No indicator is required since the end point is shown by the slightest excess of the pink-colored permanganate ion.

#### *Preparation and Standardization of Approximately 0.1 N Solutions of Potassium Permanganate and Ferrous Sulfate*

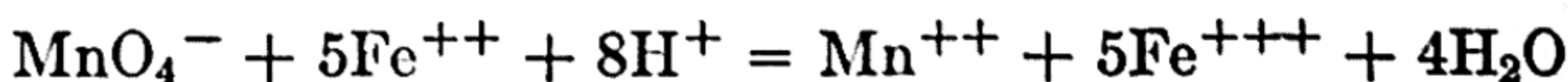
In the reaction between potassium permanganate and ferrous sulfate in the presence of acid, the manganese in the  $\text{MnO}_4^-$  ion with a valence number of  $+7$  becomes reduced to the manganous,  $\text{Mn}^{++}$ , ion, while the iron is oxidized from the ferrous,  $\text{Fe}^{++}$ , to the ferric,  $\text{Fe}^{+++}$ , state. These changes are shown by the half-cell or electron equations



and

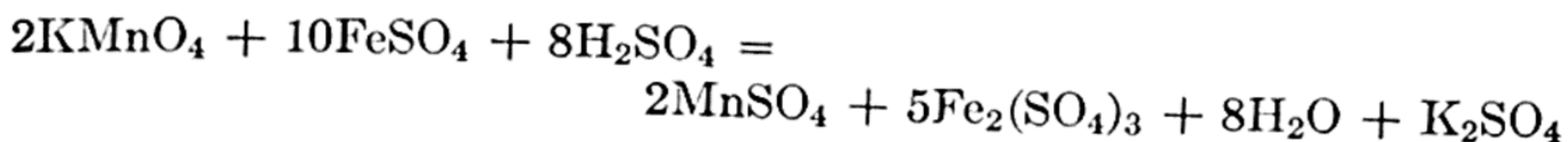


Since each  $\text{Fe}^{++}$  ion loses an electron, five  $\text{Fe}^{++}$  ions react to furnish the five needed electrons to the  $\text{MnO}_4^-$  ion. The balanced equation in ionic form, is then



This is the fundamental reaction used in the standardization of the required solutions as well as that involved in the determination of iron.

For the preparation of the permanganate solution the potassium salt,  $\text{KMnO}_4$ , is always used to supply the  $\text{MnO}_4^-$  ion; and to furnish the necessary  $\text{Fe}^{++}$  ions, either  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Mohr's salt) is employed. The reaction rewritten in molecular form is



doubling the relative proportions in order to balance the coefficients.

A normal solution of an oxidizing agent is, by definition, one that contains one gram-equivalent weight per liter and corresponds to a gain of one electron (or one unit increase in positive valence). Hence, for  $\text{KMnO}_4$ , since the change in valence is from +7 to +2, or a gain of five electrons, there is required for a liter of a normal solution, one-fifth of the molecular weight in grams (or in the above molecular equation  $2\text{KMnO}_4/10$ ). This calls for 31.61 grams of  $\text{KMnO}_4$  for a liter of solution of normal strength and 3.161 grams for a 0.1 N solution.

For a normal solution of a ferrous salt, since the valence change for the iron is from +2 to +3, or a loss of one electron, there will be required the molecular weight of the salt in grams per liter. The same conclusion can be reached by consideration of the molecular equation, because, since two gram-moles of  $\text{KMnO}_4$  react with 10 gram-moles of  $\text{FeSO}_4$  and a normal solution of  $\text{KMnO}_4$  requires a weight corresponding to  $2\text{KMnO}_4/10$ , a weight equivalent to this must be taken for the ferrous salt, that is,  $10\text{FeSO}_4/10$ , or simply  $\text{FeSO}_4$ . This corresponds to 28 grams of crystallized ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , or to 40 grams of Mohr's salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , for a liter of approximately 0.1 N solution of the reducing agent.

**Preparation of Solutions.** Weigh out about 3.25 grams of  $\text{KMnO}_4$ , dissolve it in about 900 ml. of hot water, dilute to about 1 liter, bring to a boil and boil for several minutes. Allow the solution to cool, pour it into a liter bottle and set it aside for several days.

Potassium permanganate usually contains some hydrated  $\text{MnO}_2$  which, if allowed to remain or to accumulate in the solution, causes decomposition and weakening of the solution. This impurity must be removed by filtering the solution through asbestos in the following manner. After the solution has stood for several days set up a suction flask and filter tube, place a layer of asbestos in the bottom of a large Gooch crucible and wash the asbestos with about 10 ml. of hot  $\text{KMnO}_4$  solution acidified with  $\text{H}_2\text{SO}_4$ . See page 192 for Gooch crucible assembly.

This treatment oxidizes organic matter which may be in the asbestos and which would reduce the permanganate later on. Wash the filter



free from acid, then heat the permanganate solution almost to boiling and filter hot through the asbestos. Preserve the solution in a glass-stoppered bottle, preferably one of dark glass. Guard the solution against the action of strong light and the inclusion of dust. If at any time a deposit of brown manganese dioxide is noticed the solution must be re-filtered through asbestos or else siphoned off.

To prepare the ferrous sulfate solution, weigh out on the rough balance about 40 grams of Mohr's salt (ferrous ammonium sulfate) or about 28 grams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , dissolve in distilled water, add about 5 ml. of concentrated sulfuric acid, make up to a liter and transfer to a liter bottle. The ferrous sulfate solution prepared for the dichromate procedure may, of course, be used here.

**Comparison of Solutions.** Glass-stoppered burets must be used for permanganate solutions since the rubber-tipped Mohr burets are apt to cause some reduction of the solution with consequent inaccurate results. Wash out one buret with  $\text{KMnO}_4$  solution, allow to drain and then fill with the permanganate solution. Wash out and fill another buret with the ferrous salt solution. Measure out about 30 ml. of the ferrous solution, dilute to 100 ml., add 25 ml. of "preventive solution (see page 129) and titrate with the permanganate solution, establishing the end point when the solution is faintly pink. Read the upper meniscus of the permanganate solution. Repeat the comparison.

Calculate for each comparison the number of milliliters of ferrous solution oxidized by 1 ml. of  $\text{KMnO}_4$  and also the number of milliliters of  $\text{KMnO}_4$  reduced by 1 ml. of ferrous solution. If checks are not satisfactory, repeat the entire titration. Record the data and results in the notebook.

**Selection of Method of Standardization and Determination.** Among the several methods available for the standardization of a permanganate solution the following are to be considered: (1) with iron wire, (2) with pure sodium oxalate, (3) by secondary standardization by means of an already standardized solution of a ferrous salt. If such a standard solution of ferrous sulfate is at hand (prepared in the dichromate procedure), this might of course be used here to standardize the permanganate although it is not recommended. In this case the comparison of solutions serves as a standardization.

For general purposes, standardization with pure sodium oxalate is usually recommended. It is particularly recommended here for student training, especially if time in the course does not permit making a volumetric calcium determination, since it gives practice with this important reaction. The procedure for standardization with sodium oxalate is given on page 137.

There are two alternative methods described in the following procedures for the standardization of the permanganate solution by iron wire and the application of these methods to the determination of iron in iron-containing samples. The first method described is the Zimmermann-Reinhardt method and the second the Jones reductor method. The instructor will specify which of these methods is to be employed in the standardization and in the iron ore analysis.

There are certain limitations in the application of the permanganate method to the determination of iron. If the method is to be applied to the determination of iron in iron ores, compounds of titanium and vanadium must be absent, because these elements are reduced in the Jones reductor and oxidized by permanganate; in this contingency some other reducing agent must be used. In the second place, in all titrations with permanganate, chlorides must either be absent or a modification must be introduced to overcome the effect of chlorides. Since iron ores are most readily put into solution with hydrochloric acid, the solution must either be fumed down with concentrated sulfuric acid to remove the chloride or a special reagent must be added whereby it is possible to titrate the iron in the presence of chlorides.

Chlorides, introduced into the solution through the use of hydrochloric acid as solvent, or the use of stannous chloride as reducing agent (as in the reduction of the iron in the dichromate method), interfere because some chloride ions will be oxidized, thus rendering the results high for iron. The modification followed when chlorides are present makes use of a special reagent consisting of a mixture of phosphoric acid, manganous sulfate and sulfuric acid.

#### *Zimmermann-Reinhardt Method*

This method for the standardization of a potassium permanganate solution with iron wire as well as for the determination of iron in iron samples utilizes stannous chloride for the reduction of the iron, as in the dichromate process, and embodies further the use of a special reagent mixture, known as "preventive solution," to overcome the harmful effects of chlorides. This preventive solution is made by dissolving 200 grams of manganous sulfate,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , in a liter of water and to it adding a cold mixture of 400 ml. of concentrated  $\text{H}_2\text{SO}_4$ , 400 ml. of 85 per cent  $\text{H}_3\text{PO}_4$  and 1200 ml. of water; the reagent will be supplied in the laboratory. Titration of iron solutions by potassium permanganate in the presence of chlorides gives results for iron which are too high, because some permanganate is reduced by the chloride ions. In cold solutions where the chloride concentration is low, this error may not be



very large. However, the addition of a manganous salt, in this case manganous sulfate, eliminates this difficulty by lowering the oxidation potential of the permanganate. This decreases the oxidizing action of potassium permanganate on chlorides to a negligible extent without appreciably affecting its reaction with ferrous iron.

There will also be supplied stannous chloride (50 grams dissolved in 100 ml. of concentrated HCl and diluted to a liter) and saturated mercuric chloride, to reduce excess  $\text{SnCl}_2$ .

**Standardization.** Ascertain the purity of the iron wire to be used for the standardization. Weigh out three portions of about 0.2 gram each of the cleaned wire into 500-ml. Erlenmeyer flasks, add 10 ml. of hot concentrated HCl and 10 ml. of distilled water. Cover the flasks with watch glasses and gently boil until the wire is dissolved.

Fill a buret with the permanganate solution. Wash down the sides of the flasks and watch glasses with distilled water from the wash bottle. From this point in the procedure, carry each individual solution of the standard through to the final titration before starting the reduction of the next portion.

Bring the first solution to a boil again and add stannous chloride reagent drop by drop until the solution becomes colorless or faintly green. Only a few drops may be needed. Add no more than one drop in excess. Thoroughly cool under the cold water tap and add all at once 10 ml. of saturated mercuric chloride reagent. Allow the solution to stand for three minutes. A silky, white precipitate of mercurous chloride forming at this point indicates that the procedure has been correctly followed. If no precipitate forms, too little stannous chloride was added and the iron was not completely reduced; if a black precipitate of free mercury is obtained, too great an excess of  $\text{SnCl}_2$  solution was present. In both these cases the solution must be discarded.

Add enough water to bring the volume to about 300 ml. Then add 25 ml. of the preventive reagent and titrate with permanganate without delay. The end point is reached when a pink color persists in the solution for at least half a minute.

Carry out these steps for the second portion of the iron standard in exactly the same manner. Repeat with the third portion.

To calculate the normality of the permanganate solution, divide the weight of iron standard by the volume of permanganate used and divide this in turn by 0.05584, the gram-milliequivalent weight of iron.

**Determination of Iron.** If the sample is a readily soluble salt, such as ferrous ammonium sulfate, weigh out three 0.5-gram portions into 500-ml. Erlenmeyer flasks, add 10 ml. of water and 10 ml. of concentrated HCl, heat to boiling. While hot reduce the first one with a few



drops of stannous chloride reagent dropwise and proceed with the treatment of the reduced solution, according to the instructions given below for the treatment of the solutions obtained from iron ore samples.

If the sample is an iron ore, dry it at  $110^{\circ}\text{C}$ . for one hour. Ask the instructor whether the samples contain organic material and, if so, weigh into crucibles three 0.5-gram portions; place these in a bright red muffle furnace for half an hour or heat them strongly with a Meker burner; transfer the ignited samples, without loss, to 500-ml. Erlenmeyer flasks. Should the sample not require ignition to destroy organic matter, weigh directly into the flasks.

To each flask add 20 ml. of distilled water and cover the flasks with watch glasses. Heat to boiling and then add 25 ml. of hot concentrated hydrochloric acid. Continue to heat until the ore is in solution, leaving only a small light-colored sediment of silica. A little stannous chloride aids in dissolving the ore in case the acid treatment is slow. From time to time during the dissolving of the ore, replace the acid lost by evaporation. Wash off the watch glasses and rinse down the sides of the flasks.

From this point on, each individual solution must be carried through the titration before starting to reduce the next one.

To the first hot solution add stannous chloride dropwise until the red or yellow color is discharged and the solution becomes a pale green. More of the reagent will be needed here than in the reduction of the iron wire standards. An excess of more than two drops must be avoided.

Now cool the reduced solution, whether it is from the ore or the soluble salt sample, under the water tap. Add 10 ml. of saturated mercuric chloride solution in order to oxidize the excess of stannous chloride. A silky white precipitate of mercurous chloride should form. If no precipitate is obtained, too little stannous chloride was used in the reduction and the solution must be discarded. If, on the other hand, the solution turns gray or black, showing reduced, free mercury, because too large an excess of stannous chloride was added, it must be discarded because permanganate will oxidize the mercury and results for iron will be too high.

Allow the solution to stand for three minutes.

Dilute the solution to 300 ml. with cold water, add 25 ml. of the preventive reagent and titrate without delay with the permanganate. At the end point the pink color should persist for one-half minute.

Reduce the second sample of iron, whether from soluble salt or ore, and carry the procedure through exactly as given. Repeat with the third unknown.

Calculate the percentage of iron in the sample, using both the titer and the normality methods of computation.



*Jones Reductor Method*

**Standardization of Permanganate by Iron Wire.** For the direct standardization of potassium permanganate, there are in use a number of primary standards, among which pure iron and sodium oxalate are the most satisfactory. The sodium oxalate method is described on page 137. The standardization with iron wire is here described. In getting the wire into solution some iron will become oxidized and must be reduced before the standardization titration is undertaken. A number of reducing agents are available for this preliminary reduction, such as certain metals, stannous chloride, hydrogen sulfide and sulfurous acid. In the present method, zinc in conjunction with sulfuric acid is used, because it does not introduce chlorides into the solution and does not necessitate the removal of excess reducing agent. The apparatus used is known as the Jones reductor.

A device less cumbersome than the Jones reductor has been suggested. This consists of a long spiral of cadmium, zinc or aluminum wire. In this method about 0.2500-gram portions of iron wire (electrolytic iron is more accurate) are dissolved in sulfuric acid, placed in an Erlenmeyer

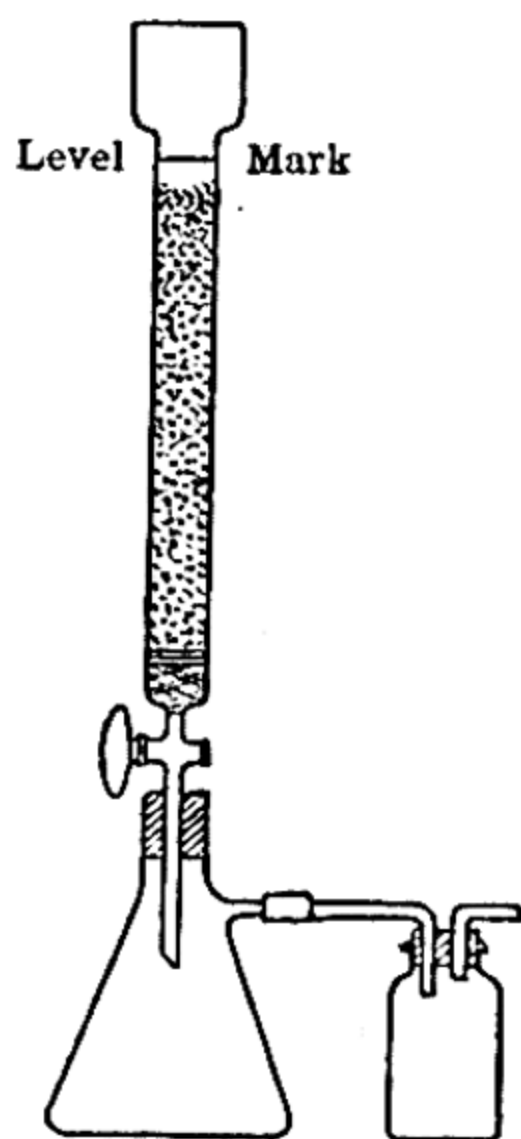


FIG. 11. Jones reductor.

flask and the spiral of metal added. Willard and Furman recommend cadmium wire or amalgamated zinc wire, 2.5 to 3 millimeters in diameter and about 1 meter long, turned into a spiral with a hook at one end so that the spiral can be removed when the reduction is complete. The solution is boiled during the reduction, and for fifteen minutes after the solution has become colorless. The spiral is then lifted out and washed off, the inside of the flask washed down and the reduced solution titrated with the permanganate solution without delay. The procedure for the determination of iron is similar to that for the standardization.

**The Jones Reductor.** This device, essentially a column of amalgamated zinc held in a vertical tube connected with a suction flask, is used here for the reduction of the iron to the ferrous state. It is illustrated

in Fig. 11. The reductor tube should have an internal diameter of about  $\frac{1}{2}$  inch and be about 18 inches long. It is enlarged at the top and has a glass stopcock sealed to the bottom. The extension beyond the stopcock should be about 6 inches long, and should be supplied with a stopper which fits snugly into the neck of the suction flask. A second suction flask or a safety bottle should be inserted in the line as a trap to



prevent water from the suction pump from backing up into the first receiver.

The amalgamated zinc is prepared as follows. Dissolve about 5 grams of mercury in about 25 ml. of dilute nitric acid, warming if necessary to start the reaction. Then dilute to 500 ml. Add to the solution 250 grams of granulated zinc of 20 to 30 mesh. Pour off the solution and wash the zinc repeatedly with water until washings are no longer acid. Preserve the zinc in a wide-mouthed bottle, under water, and use as required.

The reductor is prepared for use by placing a loose wad of glass wool in the constriction of the tube, on top of this some broken porcelain or glass and then a layer of asbestos, somewhat thicker than that used in Gooch crucibles. Then the tube is filled to a depth of 12 to 15 inches with the amalgamated zinc, and a plug of glass wool is placed on top of the zinc column and the tube is filled at once with distilled water. Place a mark on the tube about 1 inch above the upper level of the zinc column, below which the liquid level must never be allowed to fall.

The blank and the standardization can now be begun. Weigh accurately three portions of clean iron wire of about 0.2 gram each. Since the permanganate is approximately 0.1 *N*, each milliliter will oxidize about 0.005584 gram of iron, and for 40 ml. of solution there will be required about 0.2 gram. Prepare at least 1 liter of dilute sulfuric acid of about 1.1 specific gravity. Dissolve each portion of wire in 100 ml. of this dilute sulfuric acid and boil the solutions for several minutes.

**The Blank.** In order to be certain that the reductor is functioning properly and that no reducing impurities are present, a blank must be run. This consists of duplicating the exact conditions of operation, except that the iron solution is omitted. It is carried out as follows.

With the reductor properly prepared and connected with the suction flask, start the suction, partly open the stopcock at the bottom of the zinc column and slowly draw 200 ml. of distilled water through the column, being very careful not to have the water level fall below the mark above the top layer of zinc at any time. Discard the wash water.

Follow the water treatment with a total of 200 ml. of warm, dilute sulfuric acid (sp. gr. 1.1), drawing the solution through at the rate of about 25 ml. per minute. Close the stopcock when the solution level is at the mark above the top of the zinc. This precaution is very important because if air enters the column it will form hydrogen peroxide which, in turn, will act on the permanganate. Then draw 100 ml. of distilled water through the column, closing the stopcock when the water level is at the mark above the zinc. Detach the suction flask, cool the contents and quickly add a drop or two of the permanganate solution



from the buret. If the solution remains pink, the absence of foreign reducing substances is assured and the apparatus is ready for the reduction of the iron solutions; if not, repeat the acid treatment.

**The Standardization.** When a satisfactory blank is obtained, and the iron standards are dissolved and heated almost to boiling, the standardization can be completed. Pass the iron solution through the tube at the rate of about 25 ml. per minute. When the solution level has dropped to the mark, wash out the beaker which held the solution with 100 ml. of the dilute sulfuric acid and pass this through the tube. Finally follow the acid solution with 100 ml. of distilled water. Guard against allowing any portion of the zinc to be exposed to the air. Remove the flask, cool the solution and titrate without delay, until a permanent pink color is obtained. If the end point is passed, back-titrate with the ferrous sulfate solution.

Repeat this procedure with the other iron standards. Calculate the net volume of permanganate required for each run. From this calculate the Fe titer of the permanganate solution. Calculate the normality by dividing the Fe titer by the gram-milliequivalent weight of iron (0.05584).

**Procedure for Soluble Iron Salts.** Take samples of about 1 gram each, dissolve each portion in 5 ml. of concentrated  $\text{H}_2\text{SO}_4$  and 50 ml. of water, heating the solution nearly to boiling. Add 50 ml. of water. If a day or more intervenes between this analysis and the previous use of the reductor, run another blank. The procedure for the determination is the same as the standardization.

Pass the solution through the apparatus at a rate of about 25 ml. per minute. Then pass 100 ml. of dilute sulfuric acid (sp. gr. 1.1) through the column to wash out the iron solution, and follow the acid washing with 100 ml. of water, taking care that at no time the liquid level falls below the mark. Detach the suction flask, cool the reduced solution and titrate at once with standard potassium permanganate solution, using the standard ferrous sulfate solution in case the end point is passed.

From the weight of sample used and the values of the standard solutions, calculate the percentage of iron in the sample.

**Procedure for Iron Ores.** Weigh out into porcelain crucibles three portions of ore, of about 0.5 gram each. Roast the ore if necessary at a dull redness for about a half-hour, in order to oxidize carbonaceous and nitrogenous materials which may be present. Place the cooled crucibles in casseroles or evaporating dishes, add 25 ml. of dilute hydrochloric acid (sp. gr. 1.12) and heat the samples until solution is complete.

To remove the hydrochloric acid, add 5 ml. of concentrated sulfuric acid and start evaporation on the steam bath. When the solution is



clear, heat the dishes on the hot plate until white fumes of  $\text{SO}_3$  are evolved. Add not over 100 ml. of water and heat the solutions.

The reduction of the iron in the Jones reductor and the subsequent titration are carried out exactly as described above for soluble samples.

Calculate the percentage of iron in the iron ore.

### QUESTIONS

1. What reducing agents are frequently used as standard solutions in permanganate methods? In the determination of iron, explain why standard oxalic acid is not recommended.

2. What primary standards are available for the standardization of  $\text{KMnO}_4$  solution? Why use iron wire in the above method? Outline a method by which one might standardize  $\text{KMnO}_4$  indirectly.

3. What reducing agents might be used to reduce iron to the ferrous condition? Write and balance the equations for the reduction of ferric ion by (a) nascent hydrogen; (b)  $\text{SnCl}_2$ ; (c)  $\text{SO}_2$ ; (d)  $\text{H}_2\text{S}$ .

4. Write the essential reaction that takes place in the Jones reductor during the reduction of iron solutions. Why must a blank be run on the reductor? Why is it so important to prevent air from coming into contact with the zinc in the reductor? Write the reaction between  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  in  $\text{H}_2\text{SO}_4$  solution.

5. How does  $\text{KMnO}_4$  behave in neutral solution? If a certain  $\text{KMnO}_4$  solution is of normal strength in an acid solution what is its normality when used in a neutral solution?

6. Outline three methods for the determination of manganese in alloys such as steel.

### VOLUMETRIC DETERMINATION OF CALCIUM

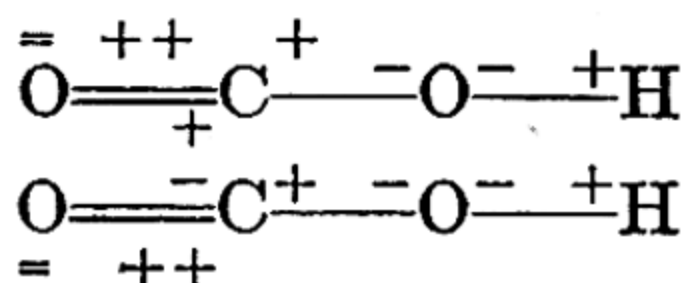
The volumetric determination of calcium is based on the precipitation of calcium oxalate, its subsequent solution in sulfuric acid and the titration of the liberated oxalate ion with a standard solution of potassium permanganate. The method is an example of those permanganate processes in which a reducing substance liberated in a suitable reaction and estimated by titration may be made the basis of a quantitative method of analysis (see page 125). The present procedure involves the preparation of standard solutions of potassium permanganate and oxalic acid and the standardization of  $\text{KMnO}_4$  by  $\text{Na}_2\text{C}_2\text{O}_4$ , which as a primary standard for  $\text{KMnO}_4$  is considered more accurate than an iron standard.

#### *Preparation and Standardization of Approximately 0.1 N Solutions of Potassium Permanganate and Oxalic Acid*

In the reaction between potassium permanganate and oxalic acid in the presence of sulfuric acid, the manganese is reduced from a valence of +7 to a valence of +2. The oxalic acid is oxidized to carbon dioxide

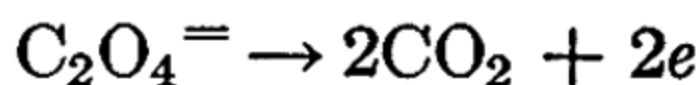


and water (when acting as a reducing agent and not as an acid). In the molecule of  $\text{H}_2\text{C}_2\text{O}_4$  the two carbon atoms have different valence charges, one atom having 4 positive charges and the other atom 3 positive and 1 negative one, as evident from the formula

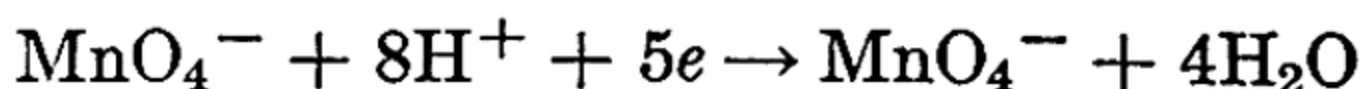


The average valence number is  $+3$ . When a molecule of  $\text{H}_2\text{C}_2\text{O}_4$  is oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  the increase in valence is 2. Since there are two carbon atoms, the average change per carbon atom is therefore an increase of 1, and for the molecule it is 2.

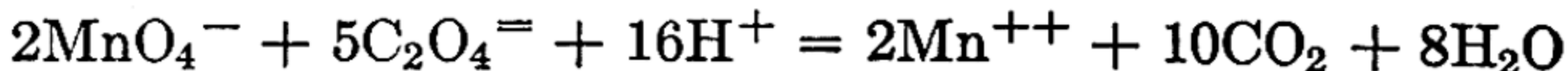
From an electron transfer standpoint we have



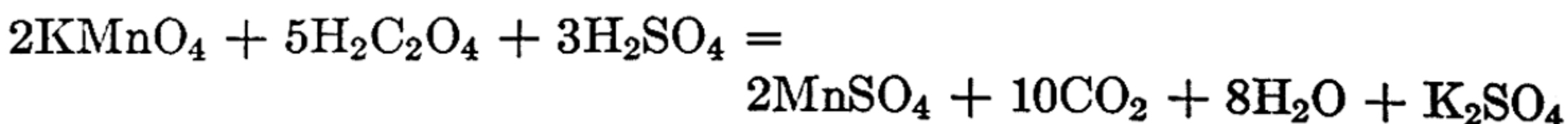
and



This leads to the balanced ionic equation



and molecularly



The reacting ratios are  $2\text{KMnO}_4 : 5\text{H}_2\text{C}_2\text{O}_4$ . A normal solution of  $\text{KMnO}_4$  contains per liter of solution one-fifth of the molecular weight in grams (in the above molecular equation  $2\text{KMnO}_4/10$ ). The weight required for a liter of normal solution is therefore 31.61 grams, and of a 0.1 *N* solution 3.161 grams, of  $\text{KMnO}_4$ .

The crystallized oxalic acid contains two molecules of water of crystallization. An oxalic acid solution, to be equivalent to this, must therefore contain  $5(\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O})/10$  or  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}/2$  gram-moles, that is, one-half the molecular weight in grams of the hydrated acid, for a normal solution. For a 0.1 *N* solution this calls for 6.3 grams per liter. If the anhydrous acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is used, there will be required 4.5 grams.

**Preparation of Solutions.** The potassium permanganate solution prepared for the determination of iron may be used here. If this solution is not at hand follow the directions given on page 127 for the preparation and purification of an approximately 0.1 *N* solution of  $\text{KMnO}_4$ .

To make a liter of approximately 0.1 *N* oxalic acid solution, weigh out about 4.6 grams of  $\text{H}_2\text{C}_2\text{O}_4$  or about 6.3 grams of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Dissolve in water, transfer to a liter flask and dilute to 1 liter.

**Comparison of Solutions.** Clean and fill a glass-stoppered buret with the permanganate solution. Clean and fill another buret with the oxalic acid solution. Run out into a 500-ml. Erlenmeyer flask an accurately measured volume of about 35 ml. of oxalic acid solution. Dilute to about 200 ml. with distilled water, add 5 ml. of concentrated sulfuric acid and titrate rapidly with the permanganate solution. Then warm to about 60°C., and add  $\text{KMnO}_4$  slowly. Near the end point add the solution drop by drop. Use the oxalic acid solution, if necessary, for back-titration. The end point is a faint, permanent pink. Read the top meniscus of the permanganate buret. Do not allow the temperature to fall below 60°C.

Repeat the comparison with another 35-ml. portion of the oxalic acid.

From the volumes of the solutions used calculate the ratio of permanganate to oxalic acid and the ratio of oxalic acid to permanganate.

**Standardization of Permanganate by Sodium Oxalate.** For the direct standardization of potassium permanganate the use of  $\text{Na}_2\text{C}_2\text{O}_4$  is recommended, and this method has the additional advantage here in that the standardization involves the same fundamental reaction as that used later in the analysis.

Weigh out three portions of the dried, pure  $\text{Na}_2\text{C}_2\text{O}_4$  supplied for standardization, of about 0.25 gram each. Dissolve each portion in about 200 ml. of water, add 5 ml. of concentrated sulfuric acid and titrate one of the solutions with the permanganate solution, adding the permanganate rapidly with continual stirring. When the end point is neared (this may be suspected by the slowness with which the solution is bleached), warm the solution to about 60°C., add the permanganate dropwise, stirring after the addition of each drop. Do not allow the solution to become cold; reheat if necessary.

Titrate the other two portions in the same manner.

From the weight of pure standard and the net volume of permanganate used, calculate the  $\text{Na}_2\text{C}_2\text{O}_4$  titer for each run. Convert the sodium oxalate titer into the  $\text{CaO}$  titer by multiplying the former by the chemical factor  $\text{CaO}/\text{Na}_2\text{C}_2\text{O}_4$ . Divide the  $\text{Na}_2\text{C}_2\text{O}_4$  titer by the gram-milliequivalent weight of  $\text{Na}_2\text{C}_2\text{O}_4$  ( $\text{Na}_2\text{C}_2\text{O}_4/2000$ ) to find the normality of the permanganate solution.

### *Determination of Calcium*

**Precipitation of Calcium Oxalate.** The precipitation of the calcium as calcium oxalate is carried out much as in the gravimetric determination of calcium (see page 201). Solutions of dilute hydrochloric acid



(sp. gr. 1.12), ammonium hydroxide (sp. gr. 0.95) and ammonium oxalate [40 grams of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  per liter] must be at hand.

Weigh out three portions of the impure calcium carbonate sample of about 0.2 gram each. Dissolve each portion in dilute hydrochloric acid, covering the beakers with watch glasses to prevent loss by spattering. Heat the solutions if action is slow. Rinse off the watch glasses and dilute the solutions to about 200 ml. Add 2 drops of methyl orange indicator. Heat to boiling and while hot add dropwise, from a pipet, 2 ml. in excess of the calculated amount of ammonium oxalate reagent. Then add dropwise, while stirring constantly, dilute ammonium hydroxide (sp. gr. 0.95) until the indicator turns yellow. No reprecipitation is necessary.

Prepare three Gooch crucibles as described under the gravimetric method for chlorides (page 192), except that they should not be dried nor brought to constant weight.

Filter the solution, first by decantation, washing the precipitates with water containing a trace of ammonium hydroxide. Transfer the precipitates to the crucibles and wash until separate portions of the filtrate no longer give a test for chlorides with silver nitrate. It is important that all ammonium oxalate be completely washed out since, if retained, it will cause high results in the subsequent titration.

When washing is complete place the crucibles in 300-ml. beakers, add 50 ml. of water, heat to almost boiling and add 5 ml. of concentrated sulfuric acid, and titrate with the standard permanganate solution. Use the standard oxalic acid solution in back-titrating if the end point is overstepped.

From the net volume of  $\text{KMnO}_4$  used, calculate the percentage of  $\text{CaO}$  in each sample.

### ADDITIONAL PERMANGANATE METHODS

Procedures for two additional permanganate processes are briefly outlined here, as optional determinations from which selection can be made. Since the titrating solutions have already been standardized the procedures are brief and not much additional time need be required for the actual determination.

#### *Analysis of Hydrogen Peroxide*

This substance reacts with  $\text{KMnO}_4$  in a sulfuric acid solution in accordance with the equation



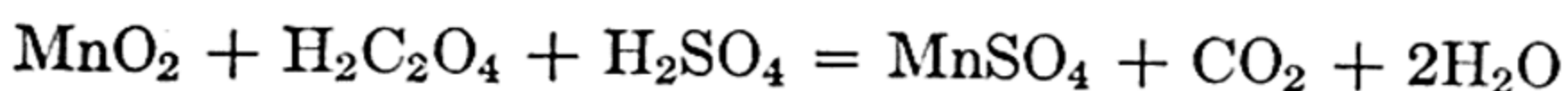
The procedure consists in taking 10 ml. of the commercial (3 per cent) hydrogen peroxide, carefully measured from a buret, and diluting it to the mark in a 100-ml. measuring flask, and measuring out in a beaker from a buret 10 ml. of this diluted solution. The solution is acidified with 25 ml. of dilute  $\text{H}_2\text{SO}_4$  and titrated with the standard solution of  $\text{KMnO}_4$  to a pink color.

From the relation  $2\text{KMnO}_4 \approx 5\text{H}_2\text{O}_2$  it is seen that the gram-milliequivalent weight of  $\text{H}_2\text{O}_2$  is  $\text{H}_2\text{O}_2/2000$ , i.e., 0.01701 gram. This is the  $\text{H}_2\text{O}_2$  titer or value of the 1 ml. of 1 N  $\text{KMnO}_4$ . The value of 1 ml. of the  $\text{KMnO}_4$  used in the titration is then 0.01701 times its normality. The weight in grams of  $\text{H}_2\text{O}_2$  in the sample titrated is determined by multiplying the volume used by the value of 1 ml. The specific gravity of hydrogen peroxide may be taken as 1, hence the weight of the original solution, in the sample titrated, is 1 gram. The percentage by weight is therefore the above product times 100.

### *Analysis of Pyrolusite*

The mineral pyrolusite is impure  $\text{MnO}_2$ . In pyrolusite ores, the impurities may be considerable. Pyrolusite formerly was an important oxidizing material and was used for making chlorine. The determination of its oxidizing power, in terms the percentage of  $\text{MnO}_2$ , is a good example of an indirect permanganate method. The method is based on adding a weighed amount of pure  $\text{Na}_2\text{C}_2\text{O}_4$ , known to be in excess, to the sample, and titrating the excess of reducing agent with standard permanganate.

Use 0.5000-gram portions of the finely ground, dried sample. Place these in beakers, weigh out accurately about 1-gram portions of pure  $\text{Na}_2\text{C}_2\text{O}_4$ , add these to the beakers, add dilute  $\text{H}_2\text{SO}_4$ , cover the beakers and heat until carbon dioxide ceases coming off and only a white residue remains. The reaction is

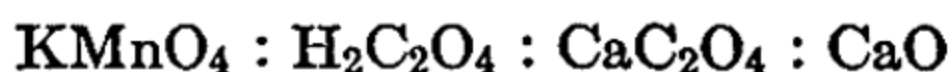


Titrate the hot solutions with an approximately 0.1 N solution of  $\text{KMnO}_4$ , to a pink color. If the end point is overstepped and a standard solution of  $\text{H}_2\text{C}_2\text{O}_4$  is at hand (from the calcium determination), use this for back-titration. From the net volume of permanganate used, the sodium oxalate unused in the reaction with the pyrolusite can be calculated and, from this, the amount required by the  $\text{MnO}_2$ . Since the change is  $\text{MnO}_2 \rightarrow \text{Mn}^{++}$ , the equivalent weight is  $\text{MnO}_2/2$ , from which the gram-milliequivalent weight and the value of 1 ml. of the  $\text{KMnO}_4$  can be calculated in terms of  $\text{MnO}_2$ . From this the purity of the ore, as percentage of  $\text{MnO}_2$ , can be readily calculated.



## QUESTIONS

1. Define a normal solution of a reducing agent. Show how the amount of oxalic acid required for a liter of normal reducing solution is determined.
2. Supply the proper divisors to make the following ratios equivalent:



3. If  $\text{KMnO}_4$  is to be employed for the analysis of impure calcium carbonate, suggest a method of standardizing such a solution other than by use of iron or sodium oxalate.
4. Devise a method for the volumetric determination of calcium in limestone, which may contain silica, compounds of iron, aluminum and magnesium in addition to  $\text{CaCO}_3$ .
5. Could you use a standard solution of ferrous salt if the end point were overstepped in the determination of calcium?

## PROBLEM SET 7

## PERMANGANATE CALCULATIONS

1. Find the normality of  $\text{KMnO}_4$  solutions containing the following weights of  $\text{KMnO}_4$  per liter: (a) 15.800 grams; (b) 2.655 grams; (c) 54.21 grams. What are the corresponding Fe titers?

*Ans.* (a) 0.5000 N; 0.02763  
 (b) 0.08401 N; 0.004691  
 (c) 1.716 N; 0.0958

2. Find (a) the Fe titer, (b) FeO titer, (c)  $\text{Fe}_2\text{O}_3$  titer of a 0.1500 N  $\text{KMnO}_4$  solution.

3. How many grams of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  should be used to prepare a liter of a solution equivalent to a  $\text{KMnO}_4$  solution containing 3.644 grams per liter?

*Ans.* 45.22

4. Find the normality of a  $\text{KMnO}_4$  solution of which 36.23 ml. is equivalent to 1.811 grams of  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .

5. A student standardized a  $\text{KMnO}_4$  solution against iron wire which is 99.8 per cent pure and found that a 0.1906-gram sample of wire required 33.85 ml. of  $\text{KMnO}_4$  solution. What is the normality of the solution? What is the Fe titer of the solution?

*Ans.* 0.1006 N; 0.005618

6. The following data were obtained by a student during an iron determination: 1.00 ml. of  $\text{KMnO}_4 \approx 1.12$  ml. of  $\text{FeSO}_4$ ; 0.2152 gram of pure iron wire required; 35.70 ml. of the  $\text{KMnO}_4$  solution and 2.65 ml. of the  $\text{FeSO}_4$  solution for back-titration. A 0.3126-gram sample of iron ore required 29.15 ml. of  $\text{KMnO}_4$  solution and 3.60 ml. of the  $\text{FeSO}_4$  solution for back-titration. What was the percentage of iron in the sample?

7. What weight of iron ore should be taken so that each milliliter of a 0.1250 N  $\text{KMnO}_4$  solution will represent 1 per cent of  $\text{Fe}_2\text{O}_3$  in the sample?

*Ans.* 0.9982 gram

8. What should be the normality of a permanganate solution in order that each milliliter used will represent 0.5 per cent of Fe in a 0.5000-gram sample?

9. A certain  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  solution has an iron titer of 0.005720. To what volume must a liter of this solution be diluted in order to make it exactly 0.1N?

*Ans.* 1024 ml.

10. A commercial hydrogen peroxide solution was analyzed by titration with potassium permanganate. A 10.00-ml. sample (sp. gr. 1.01) required 32.75 ml. of 0.5 N  $\text{KMnO}_4$ . Find the percentage of  $\text{H}_2\text{O}_2$  in the sample.

11. An ignited residue of a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , obtained in the analysis of limestone, weighed 0.3400 gram. This was fused with  $\text{KHSO}_4$  and dissolved in sulfuric acid, reduced, and the iron titrated with 0.1250 N  $\text{KMnO}_4$ , requiring 27.75 ml. Find the weight of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the sample.

*Ans.* 0.2770; 0.0630

12. Calculate the normality of  $\text{KMnO}_4$  solutions having the following titers: (a)  $\text{H}_2\text{C}_2\text{O}_4$  titer of 0.004672; (b)  $\text{CaO}$  titer of 0.02608; (c)  $\text{FeSO}_4$  titer of 0.01629.

13. What are the miliequivalent weights of the following as reducing agents:

(a)  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

(b)  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

(c)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

(d)  $\text{Na}_2\text{C}_2\text{O}_4$

*Ans.* (a) 0.06303

(b) 0.06354

(c) 0.2780

(d) 0.06700

14. If a 0.1985-gram sample of pure calcite,  $\text{CaCO}_3$ , is used in standardizing a  $\text{KMnO}_4$  solution, and 33.78 ml. of the permanganate solution are required, what is (a) the normality, (b) the  $\text{CaCO}_3$  titer, (c) the  $\text{CaO}$  titer, and (d) the  $\text{Ca}$  titer of the permanganate solution?

15. It was found that 25.00 ml. of a certain  $\text{H}_2\text{C}_2\text{O}_4$  solution was neutralized by 28.70 ml. of a 0.1000 N  $\text{NaOH}$  solution. Find the normality of a  $\text{KMnO}_4$  solution, 33.75 ml. of which reacts with 30.35 ml. of the  $\text{H}_2\text{C}_2\text{O}_4$  solution.

*Ans.* 0.1032 N

16. The calcium in a 0.1984-gram sample of limestone was precipitated as  $\text{CaC}_2\text{O}_4$ . This was then dissolved in sulfuric acid and titrated with 29.64 ml. of  $\text{KMnO}_4$  which had a  $\text{Na}_2\text{C}_2\text{O}_4$  titer of 0.006480. What was the percentage of  $\text{CaO}$  in the limestone?

17. The  $\text{CaO}$  titer of a certain  $\text{KMnO}_4$  solution is 0.003806. How many grams of  $\text{K}_2\text{Cr}_2\text{O}_7$  must be taken to make a liter of potassium dichromate of the same strength?

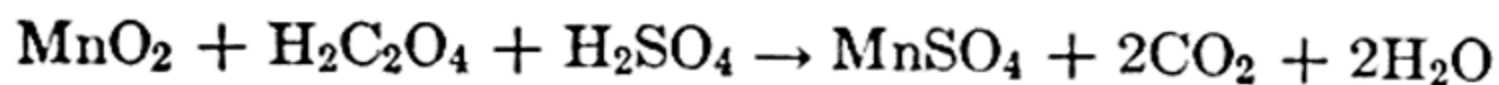
*Ans.* 6.653 grams

18. How much water should be added to a liter of  $\text{KMnO}_4$  solution having a  $\text{CaO}$  titer of 0.002912 which is to be used for oxidation in an acid medium in order to make the solution 0.1000 N?

19. The following substances were mixed: 35 ml. of 0.1000 N  $\text{KMnO}_4$  solution, 3.50 grams of  $\text{Na}_2\text{C}_2\text{O}_4$ , and 4.30 grams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The mixture was diluted to 250 ml. and acidified with  $\text{H}_2\text{SO}_4$ . Show by a calculation whether the resulting solution is oxidizing or reducing.

*Ans.* Reducing

20. Pyrolusite (impure  $\text{MnO}_2$ ) is analyzed by treating the mineral with a known excess of reducing agent in the presence of acid and then back-titrating the reducing agent with standard  $\text{KMnO}_4$  solution. The first reaction is described by the equation



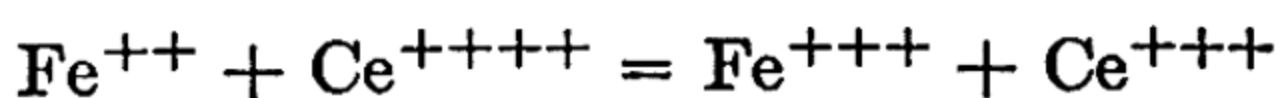
Calculate the percentage of  $\text{MnO}_2$  in a sample from the following data. A 0.2200-gram sample was treated with 50.00 ml. of 0.1024 N  $\text{H}_2\text{C}_2\text{O}_4$  solution in the presence of sulfuric acid. The excess oxalic acid was titrated with 36.75 ml. of 0.1096 N  $\text{KMnO}_4$  solution.

### C. CERIC SULFATE METHODS

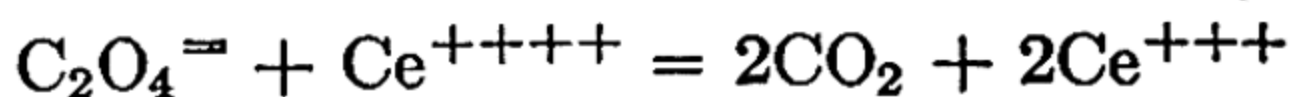
Ceric sulfate,  $\text{Ce}(\text{SO}_4)_2$ , a newcomer to the group of strong standard oxidizing reagents, is in many respects similar to potassium permanga-



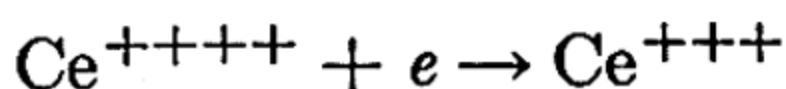
nate. In oxidizing power it is nearly as strong as the latter and stronger than potassium dichromate. In the reaction with ferrous ion



and with oxalates



the change in valence is from +4 to +3 or a change of one unit.



The equivalent weight is therefore the atomic weight, and to make a 0.1 *N* solution, one-tenth of the gram-molecular weight of the salt should be taken.  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  is usually used to prepare the solution; this has a molecular weight of 632.5; therefore about 63 grams are taken, dissolved in 25 ml. of concentrated  $\text{H}_2\text{SO}_4$  and diluted to 1 liter for a 0.1 *N* solution. This is best standardized against pure iron as primary standard or, indirectly, against a previously standardized solution of  $\text{FeSO}_4$ . In the standardization and reactions with iron, orthophenanthroline is used as indicator, changing color from red to blue or purple. The indicator, when in a ferrous solution, consists of the probable complex,  $\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3^{++}$  and, when oxidized, of  $\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3^{+++}$ . The reactions, unlike those with permanganate, can be conducted in the presence of hydrochloric acid.

In carrying out reactions of iron with ceric sulfate, the iron is reduced with  $\text{SnCl}_2$  as in the dichromate or permanganate method.

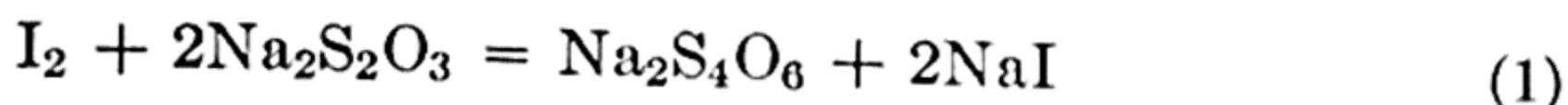
The titration then proceeds according to the procedures already described.

#### D. IODINE METHODS

Volumetric methods of analysis based upon the reactions of iodine and its compounds are extensively employed in analytical chemistry. Iodine methods constitute by far the most important and largest class of volumetric procedures. Three forms of the element iodine—namely, the free element,  $\text{I}_2$ , the iodide ion usually introduced as  $\text{KI}$  and the iodate ion used in the form of its potassium salt,  $\text{KIO}_3$ —are employed. Iodine is a good oxidizing agent and can be used as a standard solution to oxidize directly a number of reducing substances. The iodide ion,  $\text{I}^-$ , is an excellent reducing agent and reacts with a large number of oxidized substances to liberate free iodine, which may then be measured by titration with a standard reducing agent. Potassium iodate is a good oxidizing agent and may be used directly as a standard solution or in a mixture with potassium iodide. In most of the iodine methods starch

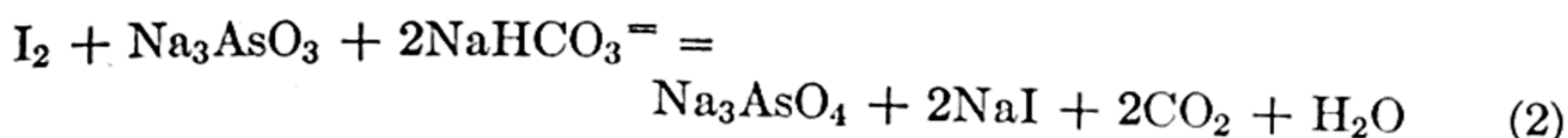
is used as indicator; it gives an intense blue color in the presence of a slight excess of free iodine.

**Fundamental Reactions.** Iodine reacts quantitatively with sodium thiosulfate, according to the equation



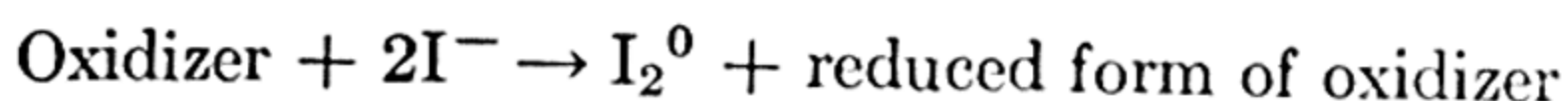
This reaction when applied to titration procedures is one of the most accurate and best-suited reactions of quantitative analysis. The completion of the reaction is admirably marked by the starch indicator.

Another fundamental reaction is that between iodine and the arsenite ion,  $\text{AsO}_3^=$ , the reaction being quantitatively complete in the presence of sodium bicarbonate:



Starch indicator is likewise used in this reaction.

These two reactions are of considerable importance because they are used to measure the amount of iodine liberated by the action of an oxidizing agent on potassium iodide. The action of an excess of (unstandardized) potassium iodide on a substance capable of being reduced can be shown schematically thus:



the liberated iodine being then titrated by a standard solution of either sodium thiosulfate or sodium arsenite. The amount of standard reducer used becomes then a measure of the amount of oxidizer contained in the sample.

**Classification of Iodimetric Methods.** 1. Methods of analysis which depend upon the consumption of iodine are termed iodimetric methods. Such methods are carried out either directly by titrating the constituent being determined with a standard solution of iodine, or indirectly by adding a measured excess of standard iodine and back-titrating the excess with a standard solution of sodium arsenite or sodium thiosulfate.

2. Reactions in which iodine is liberated from potassium iodide by the action of the constituent being determined and the iodine then titrated by a standard solution of sodium thiosulfate or sodium arsenite are called iodometric methods.

3. Iodate methods employ a standard solution containing  $\text{KIO}_3$  either alone or in admixture with  $\text{KI}$ . Closely allied to the iodate methods are those that employ potassium bromate. Time and space do not permit describing these methods in detail nor offering laboratory procedures involving these interesting methods. They are briefly summarized on page 155.



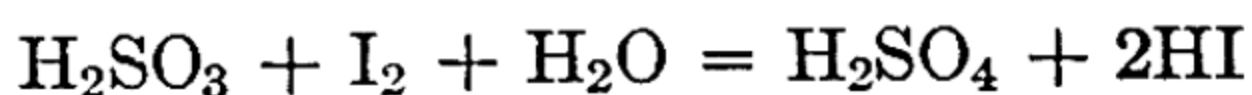
### METHODS INVOLVING THE CONSUMPTION OF IODINE (IODIMETRIC METHODS)

As already pointed out, certain materials in the lower state of oxidation can be quantitatively oxidized by iodine. The sample may either be titrated directly with a standard solution of iodine, or else an excess of standard iodine may be added and the excess back-titrated by means of standard arsenite or thiosulfate solution. In either case, the determination rests upon the direct oxidation of the constituent by standard iodine.

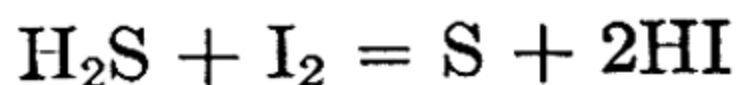
For example the reaction between iodine and sodium thiosulfate may become an accurate method for the determination of thiosulfates by titration of the sample with an iodine solution. (Conversely, free iodine in a sample of material may be determined by titration with standard thiosulfate.)

In a similar manner, the reaction between iodine and the arsenite ion in a sodium bicarbonate solution is the basis for a direct iodimetric determination of trivalent arsenic. This method is described in detail in the following procedure. Determinations of antimony and tin are based on similar reactions.

Sulfites may be oxidized by iodine, according to the reaction



Likewise, sulfides, by the reaction



The latter reaction is involved in the so-called evolution method for the determination of sulfides in steel. In actual practice, the steel is dissolved in hydrochloric acid and the evolved hydrogen sulfide is passed into cadmium chloride or zinc sulfate solution, by which the hydrogen sulfide is retained as CdS or ZnS. The precipitated sulfide is then dissolved in an acidified solution containing an excess of standard iodine and the excess back-titrated with thiosulfate solution or, alternatively, titrated directly with standard iodine or iodate.

The determination of arsenic in impure arsenious oxide samples is selected as a typical example of a direct iodimetric method and will give practice in the use of iodine and arsenite solutions.

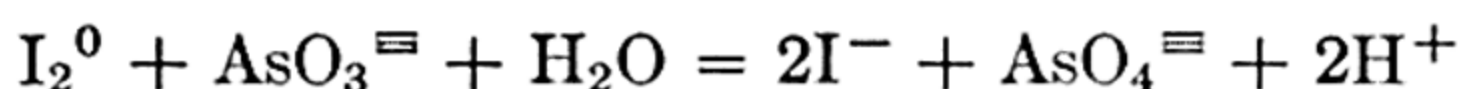
### VOLUMETRIC DETERMINATION OF ARSENIC

The method is based on the oxidation of arsenic from the arsenious to the arsenic state, by direct titration with standard iodine. The determination involves the preparation and standardization of solutions of

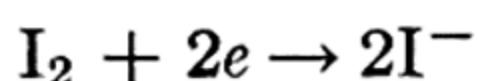
iodine and sodium arsenite, which are then used in the determination of arsenic in samples of impure  $\text{As}_2\text{O}_3$ .

*Preparation and Standardization of Approximately 0.1 N Solutions  
of Iodine and Sodium Arsenite*

In the reaction



the iodine is reduced to the iodide ion, each atom of iodine undergoing a valence change of 1, because in the reaction

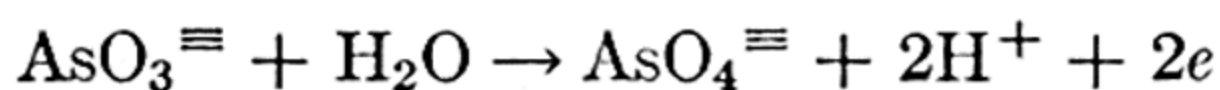


each atom of iodine gains one electron. A normal solution of iodine therefore contains the atomic weight of iodine in grams per liter. A liter of one-tenth normal solution of iodine will contain one-tenth the atomic weight of iodine or 12.693 grams. The solubility of iodine in water is slight but it dissolves readily in a solution of potassium iodide. When iodine dissolves in potassium iodide, it probably does so according to the reaction

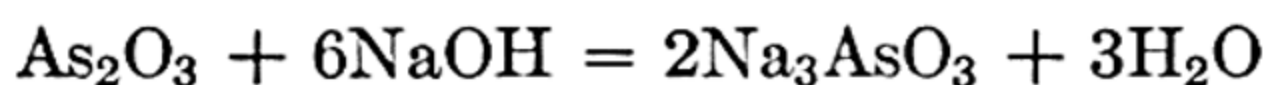


forming the double salt  $\text{KI} \cdot \text{I}_2$  which ionizes into  $\text{K}^+$  ion and the tri-iodide ion,  $\text{I}_3^-$ . A solution of iodine in potassium iodide behaves like  $\text{I}_2$  and will be so regarded here.

A solution of an arsenite, in order to be normal as a reducing agent, must contain the gram-equivalent weight per liter of solution. When the  $\text{AsO}_3^{\equiv}$  ion is oxidized to  $\text{AsO}_4^{\equiv}$  the valence change is 2, since two electrons are lost, as can be seen from the half-cell reaction

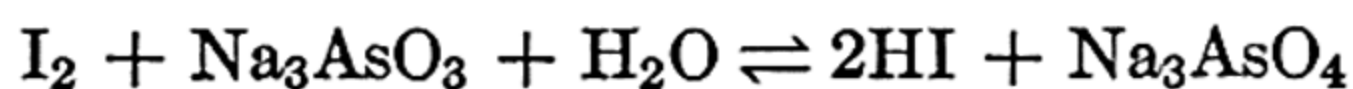


Therefore a normal solution contains one-half the molecular weight of the compound in grams per liter. The starting material for a sodium arsenite solution is usually arsenious oxide. This dissolves in sodium hydroxide, as shown in the equation



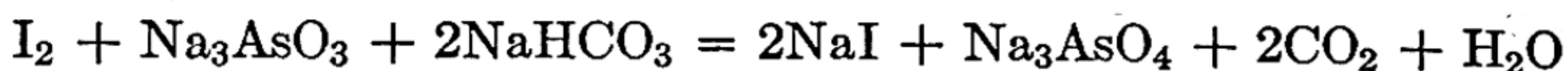
Since in a molecule of  $\text{As}_2\text{O}_3$  there are two arsenic atoms, each of which changes valence from +3 to +5 on being oxidized, there is required one-fourth the gram-molecular weight of arsenious oxide per liter for a normal solution. For a liter of normal solution there are required therefore  $\text{As}_2\text{O}_3/4 = 197.82/4 = 49.45$  grams and for a 0.1 N solution 4.95 grams.

The reaction between iodine and sodium arsenite





is decidedly reversible and reaches equilibrium while still large amounts of arsenite remain in the solution, owing to the interaction of hydriodic acid with the arsenate ion. If means are taken to prevent the hydrogen-ion concentration from building up, the reaction can be made to go to practical completion in the desired direction. Such a means is available in a sodium bicarbonate buffer, the action of the bicarbonate being to neutralize the HI as fast as it is formed. In the presence, then, of sodium bicarbonate, the following reaction is satisfactorily quantitative:



**Preparation of Solutions.** It is possible to make a solution of iodine of the exact desired strength, from carefully purified and resublimed iodine, with the exercise of extreme care to prevent loss. For the present purpose, however, it is better to make the solution of an approximate strength and to standardize it against pure  $\text{As}_2\text{O}_3$ .

For a liter of an approximately 0.1 *N* solution of iodine, weigh out about 13 grams of iodine and 20 grams of KI. Rub these together in a mortar with small portions of water until dissolved. Transfer the solution to a liter flask, make up to 1 liter. Transfer the solution to a liter bottle. This should be sufficient for this and the following copper determinations. Wrap dark paper around the bottle (an amber-colored bottle is better) to protect the solution from decomposition by direct sunlight.

For 500 ml. of an approximately 0.1 *N* solution of sodium arsenite, weigh out about 2.5 grams of arsenious oxide. Prepare a sodium hydroxide solution by dissolving 20 grams of NaOH in 250 ml. of water. Add enough of the sodium hydroxide to the arsenious oxide to dissolve it (10 ml. should be sufficient). Dilute to 500 ml. and transfer to a liter bottle.

If starch indicator solution is not supplied, prepare a quantity by rubbing about 1 gram of potato or soluble starch into a paste with cold water and then pouring this into about 100 ml. of boiling water. Set the solution aside for some time and then decant the clear solution.

**Comparison of Solutions.** Measure from a buret about 35 ml. of the sodium arsenite solution. Dilute to 100 ml. Add a drop of phenolphthalein and then dilute hydrochloric acid (sp. gr. 1.12). The phenolphthalein indicator may show an abnormal behavior in that, when first added to the above solution, it is colorless even in an alkaline solution, and addition of acid will show a color change first to pink and then to colorless. Add a few drops of acid in excess of the neutrality point. Dilute the solution to 150 ml., provide a cover for the flask and add 7 grams of sodium bicarbonate, covering the flask at once to prevent loss by effervescence. Wash the cover glass and sides of the flask. Run into



the flask from a glass-stoppered buret about 30 ml. of the iodine solution, add 2 ml. of the starch indicator and titrate to the appearance of a permanent blue color.

Repeat the comparison with fresh portions of the solutions.

Calculate the number of milliliters of arsenite reduced by 1 ml. of the iodine solution.

**Standardization of the Iodine Solution by  $\text{As}_2\text{O}_3$ .** Arsenious oxide is a satisfactory primary standard for the direct standardization of iodine. The oxide can be procured in a high state of purity. A gram portion should be dried in a drying oven to be certain that it is free from moisture, unless that supplied has already been dried.

Weigh out into 250-ml. Erlenmeyer flasks three portions of about 0.2 gram each. Dissolve each portion in 10 ml. of the dilute sodium hydroxide. Dilute to 100 ml., add a drop of phenolphthalein indicator, neutralize with dilute hydrochloric acid and add three drops in excess.

Dilute the slightly acid solutions to 150 ml., add 7 grams of  $\text{NaHCO}_3$ , cover with watch glasses until action is over and then wash down the sides of the flasks and the cover glasses. Calculate the number of milliliters of 0.1 *N* iodine required to oxidize 0.2 gram of  $\text{As}_2\text{O}_3$ . Add from a buret about 5 ml. less than the required amount, add 2 ml. of starch solution and titrate to the end point. If the end point is passed, back-titrate with the sodium arsenite solution.

From the net volume of iodine required and the comparison data calculate the normalities of both solutions.

**Determination of Arsenious Oxide.** Weigh out portions of the impure  $\text{As}_2\text{O}_3$  samples of about 0.25 gram each. Dissolve each portion in 10 ml. of dilute sodium hydroxide solution. Dilute to 100 ml., add phenolphthalein indicator and neutralize with dilute hydrochloric acid, adding three drops in excess.

Make up the volume to 150 ml. with water, add 7 grams of sodium bicarbonate and titrate with the standard iodine solution, adding the starch indicator after 15 or 20 ml. of the iodine have been added. If the end point is passed, back-titrate with standard sodium arsenite solution.

Calculate the percentage of  $\text{As}_2\text{O}_3$  in the sample.

## QUESTIONS

1. Name four reducing substances which may be determined by direct titration with iodine. Supply the equations for the reactions involved.

2. What precautions must be observed in making up and preserving a solution of iodine? Why dissolve the iodine in potassium iodide?

3. Explain how  $\text{NaHCO}_3$  acts as a buffer during the titration of arsenites by iodine. Why is the addition of  $\text{NaHCO}_3$  required? Why not use  $\text{NaOH}$ ?



4. How might one standardize a solution of iodine other than by pure  $\text{As}_2\text{O}_3$ ?
5. Outline a method for the determination of hydrogen sulfide.
6. Explain the action of starch as an indicator and give reasons for the care required in its preparation.

### PROBLEM SET 8

#### CALCULATIONS INVOLVING THE CONSUMPTION OF IODINE

1. Calculate the milliequivalent weights of the following: (a) iodine; (b)  $\text{Na}_3\text{AsO}_3$ ; (c)  $\text{As}_2\text{O}_3$ .  
 Ans. (a) 0.1269  
 (b) 0.09595  
 (c) 0.04946
2. What weight of pure  $\text{As}_2\text{O}_3$  should be used when standardizing a 0.1000 *N* iodine solution so that not more than 35.00 ml. of iodine solution will be used during the titration?
3. If 27.25 ml. of a 0.1356 *N* iodine solution is found to react with 28.75 ml. of a  $\text{Na}_2\text{AsO}_3$  solution, what is the normality of the arsenite solution?     Ans. 0.1285 *N*
4. How much water must be added to 950 ml. of a 0.1026 *N* iodine solution in order to make a solution which is exactly 0.1000 *N*?
5. Calculate the percentage of  $\text{As}_2\text{O}_3$  in a sample of material if a 0.2200-gram sample requires 37.32 ml. of 0.1138 *N* iodine solution.     Ans. 95.5 per cent
6. In what proportions should 0.1048 *N* and 0.00987 *N*  $\text{Na}_3\text{AsO}_3$  solutions be mixed to give a 0.1000 *N* solution?
7. It is found that 26.41 ml. of a  $\text{Na}_3\text{AsO}_3$  solution reacts with 30.12 ml. of a 0.1236 *N* iodine solution. What is the sulfur titer of the  $\text{Na}_3\text{AsO}_3$  solution?  
 Ans. 0.002260
8. What is the percentage of  $\text{As}_2\text{O}_3$  in a sample of disodium arsenite, if 32.65 ml. of 0.1136 *N*  $\text{I}_2$  are used in titrating a 0.1975-gram sample?
9. A 1.500-gram sample of steel was treated with  $\text{HCl}$ , the evolved  $\text{H}_2\text{S}$  precipitated as  $\text{CdS}$  and the  $\text{CdS}$  dissolved in an acidified solution containing 50.00 ml. of 0.1250 *N* iodine solution. The excess iodine was titrated with 45.65 ml. of 0.1236 *N*  $\text{Na}_3\text{AsO}_3$  solution. Calculate the percentage of sulfur in the steel.  
 Ans. 0.650 per cent
10. Calculate the  $\text{As}_2\text{O}_3$  titer of a 0.1682 *N*  $\text{Na}_2\text{AsO}_3$  solution. Calculate the normality of an arsenite solution having an  $\text{As}_2\text{O}_3$  titer of 0.1865.
11. A student secures the following data during an arsenious oxide analysis:  
 Comparison of solutions  
 34.69 ml.  $\text{I}_2 \approx$  36.81 ml.  $\text{Na}_3\text{AsO}_3$   
 Standardization  
 Weight of  $\text{As}_2\text{O}_3$      = 0.2212 gram  
 Volume of  $\text{I}_2$          = 38.47 ml.  
 Volume of  $\text{Na}_3\text{AsO}_3$  = 3.82 ml.  
 Analysis  
 Weight of sample     = 0.2882 gram  
 Volume of  $\text{I}_2$          = 31.28 ml.  
 Volume of  $\text{Na}_3\text{AsO}_3$  = 2.50 ml.  
 Calculate the percentage of  $\text{As}_2\text{O}_3$  in the sample.     Ans. 63.64 per cent
12. Calculate the percentage of antimony in a stibnite ( $\text{Sb}_2\text{S}_3$ ) ore, 0.5623 gram of which requires 33.26 ml. of a 0.1324 *N* iodine solution.

13. What is the percentage of  $\text{As}_2\text{O}_3$  in a sample of paris green if a 0.4000-gram sample required 37.51 ml. of a 0.1100 *N* solution of iodine for the oxidation of the arsenic? *Ans.* 51.12 per cent

14. What is (a) the  $\text{H}_2\text{SO}_3$  titer, (b) the  $\text{Na}_2\text{SO}_3$  titer, (c) the  $\text{SO}_2$  titer of a 0.2000 *N* solution of iodine?

15. How much water must be added to 875 ml. of a 0.2167 *N* iodine solution in order to make an exactly 0.2000 *N* solution? *Ans.* 73.1 ml.

16. Calculate the *S* titer of a  $\text{Na}_3\text{AsO}_3$  solution, 41.26 ml. of which reacted with 40.00 ml. of a 0.1362 *N* solution of iodine.

17. If a certain iodine solution is 0.2126 *N*, what weight of  $\text{Na}_3\text{AsO}_3$  should be added to 500 ml. of this solution in order to make it exactly 0.2000 *N*? *Ans.* 0.6045 gram

18. Calculate the percentage of antimony in a sample of antimony ore, which on analysis required 32.65 ml. of an iodine solution, the latter having been standardized by causing 0.1478 gram of pure  $\text{As}_2\text{O}_3$  to react with 30.00 ml. of the iodine. The weight of antimony ore was 0.9637 gram.

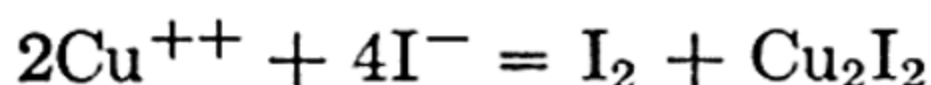
19. What would be a suitable weight of pure resublimed iodine to use for the standardization of an approximately 0.01 *N* solution of  $\text{Na}_3\text{AsO}_3$ , if not more than 40.00 ml. is to be used? *Ans.* 0.0508 gram

20. A 5.000-gram sample of steel was dissolved in  $\text{HCl}$  and the  $\text{H}_2\text{S}$  absorbed in an ammoniacal  $\text{ZnSO}_4$  solution. The precipitated  $\text{ZnS}$  was dissolved in the presence of 25.00 ml. of 0.03568 *N* iodine. The excess iodine was then titrated with 0.03662 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  requiring 18.55 ml. Calculate the percentage of sulfur in the steel. *Ans.* 0.068 per cent

### METHODS INVOLVING THE LIBERATION OF IODINE (IODOMETRIC METHODS)

In the iodometric methods considered in the present section, the amount of iodine liberated by the action of potassium iodide on the substance being analyzed is made the basis of the method. In methods of this kind, the sample must be in the oxidized form and is reduced by  $\text{KI}$ . The liberated iodine is then titrated with a standard solution of sodium thiosulfate or sodium arsenite, using starch as indicator. This type of method allows much variation in experimental arrangement so that a greater number of determinations can be carried out by this indirect iodimetric method than by any other volumetric method. Two such variations in technique are discussed below.

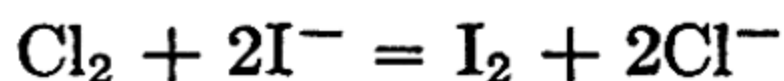
In the first place, an excess of strong potassium iodide solution may be allowed to react directly with the material under analysis, the free iodine being titrated with standard reducer. As the first example under this head may be mentioned the determination of copper, which is based on the reaction



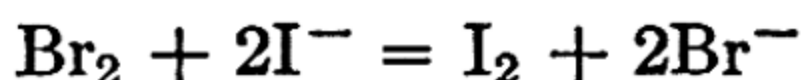
and for which the procedure is given in detail below.



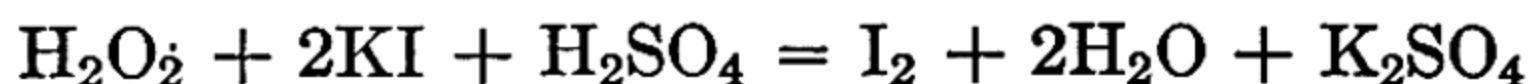
Free chlorine and free bromine may be determined by similar reactions:



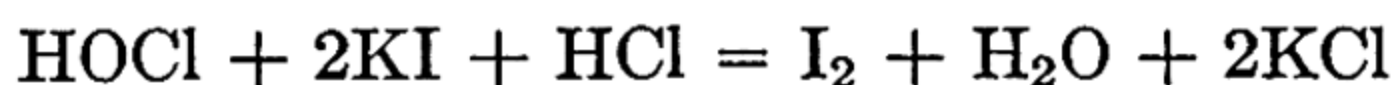
and



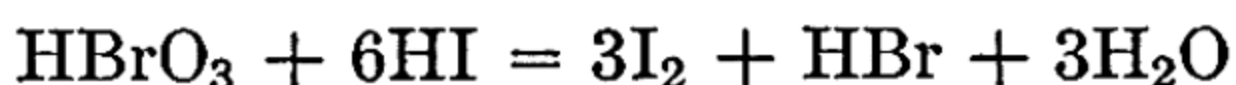
Hydrogen peroxide reacts with KI to liberate iodine as shown by the equation



Hypochlorites in presence of HCl will liberate iodine from potassium iodide:



Bromates may be satisfactorily determined by a method based on the reaction



in solutions not too strongly acid with HCl.

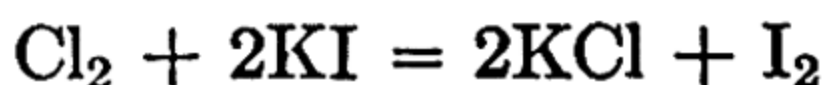
Permanganates, dichromates and chromates react in acid solutions with potassium iodide, and may be determined by such reactions. Use may be made of standard solutions of  $\text{KMnO}_4$  or of  $\text{K}_2\text{Cr}_2\text{O}_7$  to standardize a  $\text{Na}_2\text{S}_2\text{O}_3$  solution by the intermediate liberation of iodine.

Certain indirect determinations may be carried out by allowing the material, in the oxidized form, to react with HCl or HBr, by which free chlorine or free bromine is evolved, which in turn is passed into strong potassium iodide solution, and the iodine thus liberated is titrated with standard reducer. The method is applicable to the determination of such substances as manganese dioxide, nitrates, nitrites, vanadates, etc.

As an example, the analysis of pyrolusite, the ore of manganese dioxide, may be cited. The sample is treated with HCl in a reaction flask, when the following reaction takes place:



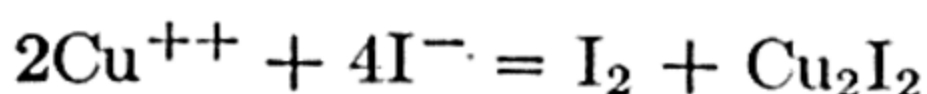
The chlorine is passed into a receiver which contains a strong solution of KI:



and the iodine liberated is titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Compare this method for the analysis of pyrolusite with the permanganate method previously described on page 139.

## VOLUMETRIC DETERMINATION OF COPPER

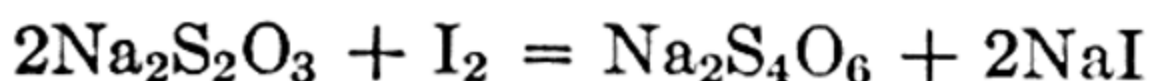
This procedure is an example of an iodometric determination in which iodine is liberated from potassium iodide and titrated with standard sodium thiosulfate solution. The copper is reduced from the cupric to the cuprous state, being precipitated as cuprous iodide in accordance with the reaction



The method is applicable to the determination of copper in cupric compounds and, by modifications, can be applied to the determination of copper in ores, minerals and alloys. Provision is made below for both types of samples. The procedure calls for standard solutions of sodium thiosulfate and iodine.

*Preparation and Standardization of Approximately 0.1 N Solutions of Iodine and Sodium Thiosulfate*

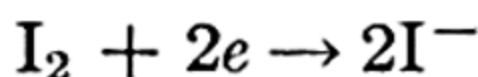
In the reaction



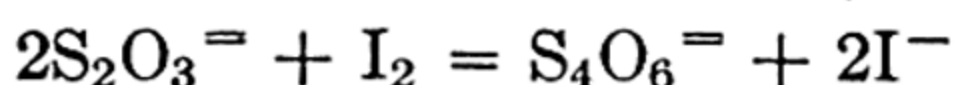
the sodium thiosulfate is oxidized to sodium tetrathionate and the iodine is reduced to sodium iodide. The half-cell reactions are



and



giving the balanced ionic equation



From these electron equations it is seen that an equivalent weight of iodine is one-half the molecular weight or, directly, the atomic weight, and a gram-equivalent weight therefore is 126.93 grams. A liter of 0.1 N solution of  $\text{I}_2$  hence contains 12.693 grams of iodine.

In the oxidation of  $2\text{S}_2\text{O}_3^{=}$  to  $\text{S}_4\text{O}_6^{=}$  two electrons are involved, hence the gram-equivalent weight of  $\text{Na}_2\text{S}_2\text{O}_3$  is  $2\text{Na}_2\text{S}_2\text{O}_3/2$  or directly the gram-molecular weight (158.11 grams) of the anhydrous salt. The salt to be used is  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ; therefore, 248.2 grams of the crystallized pentahydrate in a liter of solution will give a normal solution of this reagent, and one-tenth of this amount (24.82 grams) should be used for a 0.1 N solution.

This fact can be independently deduced from valence considerations alone. In the molecule of  $\text{Na}_2\text{S}_2\text{O}_3$  one sulfur atom has a valence of +6, the other a valence of -2, the average valence being +2. In  $\text{Na}_2\text{S}_4\text{O}_6$ ,



two sulfur atoms each have an apparent valence of  $+6$ , the third  $0$  and the fourth  $-2$ , the average valence number being  $+2\frac{1}{2}$ . There is therefore an average apparent valence increase of  $+\frac{1}{2}$  for each atom of sulfur; and, since two atoms of sulfur are contained in one molecule of  $\text{Na}_2\text{S}_2\text{O}_3$ , the gram-molecular weight per liter will give a normal solution of this reagent.

**Preparation of Solutions.** The solution of iodine used for the analysis of arsenious oxide should be used here if available. If not, make up the iodine solution as follows: Grind together in a mortar about 13 grams of pure iodine and 20 grams of KI with a little water. When dissolved, transfer to a liter flask and fill to the mark with distilled water. Store the iodine solution in a dark-colored or paper-wrapped bottle, since it is acted upon by strong sunlight.

Make a liter of approximately  $0.1\text{ N}$  sodium thiosulfate solution by dissolving 25 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in freshly boiled and cooled distilled water. This boiling and cooling of the water is necessary to free it from carbon dioxide, the presence of which would gradually decompose sodium thiosulfate.

Prepare starch indicator solution as directed on page 146 unless already prepared and available in the laboratory.

Prepare a solution of potassium iodide by dissolving 30 grams of KI in water and diluting to 100 ml. A solution of KCNS containing 20 grams per 100 ml. will be supplied.

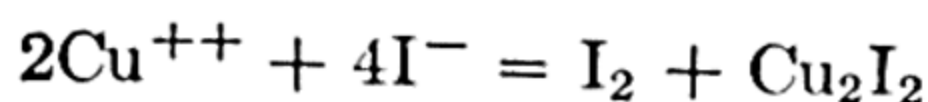
**Comparison of Solutions.** Place the iodine in a buret provided with a glass stopcock, since rubber is attacked by strong oxidizing agents. From the other buret run out about 35 ml. of the thiosulfate solution, dilute to about 150 ml., add 2 ml. of the starch indicator and then add iodine until a permanent blue color is produced. Add thiosulfate solution if the end point has been passed.

Calculate the number of milliliters of thiosulfate oxidized by 1 ml. of iodine and likewise the volume of iodine used by 1 ml. of thiosulfate solution. Repeat the comparison until satisfactory agreement in the ratios is obtained.

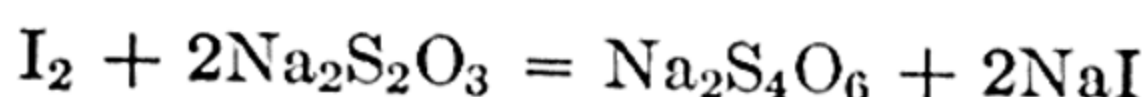
Obviously, if the iodine solution is the one already prepared and standardized for the arsenic determination and not separately prepared for the copper determination, this comparison constitutes, at the same time, by proper calculation, a standardization of the thiosulfate solution. It is nevertheless recommended that the thiosulfate solution be independently standardized according to the following procedure.

**Standardization of the Thiosulfate Solution by Copper.** Thiosulfate solutions may be standardized in a number of ways as, for instance, directly against pure iodine or a standardized solution of iodine, against

potassium bromate, permanganate, dichromate or against pure copper. The last-named standard is preferable in the present instance, since the solution is to be used for the determination of copper. The method depends upon the liberation of iodine from KI by a known weight of pure copper, and the subsequent titration of the iodine with the thiosulfate solution. The reactions involved are



and



From the relationships,  $2\text{Cu}^{++} \approx \text{I}_2 \approx 2\text{Na}_2\text{S}_2\text{O}_3$ , the gram-equivalent weight of copper is 63.57, and the gram-milliequivalent weight is 0.06357. Hence the copper titer of a tenth-normal solution is 0.006357. If 35 ml. of the thiosulfate are anticipated for standardization, a suitable weight of pure copper to use would be  $35 \times 0.006357$  or about 0.22 gram.

Weigh out accurately and place in 250-ml. Erlenmeyer flasks three portions of pure copper in the form of foil or wire, of 0.2 to 0.25 gram each. To each flask add 3 to 5 ml. of concentrated  $\text{HNO}_3$  and an equal volume of water, warming if necessary until the metal is dissolved. When it is dissolved add 15 ml. of water and 5 ml. of the urea solution supplied. This reagent was prepared by dissolving 50 grams of urea in a liter of water and is used to eliminate oxides of nitrogen. Boil for a minute and cool.

Add dilute ammonia solution dropwise to the cooled solutions until a precipitate of  $\text{Cu}(\text{OH})_2$  begins to form. If too much ammonium hydroxide is added as shown by an intense deep blue color of the solution, carefully add a few drops of dilute  $\text{HNO}_3$  and again cautiously neutralize with ammonia solution.

Add to the solution 1 gram of potassium acid phthalate and allow it to dissolve. This reagent will keep the solution at the proper acidity for titration with the thiosulfate solution.

Fill a buret with the thiosulfate solution, in readiness for the standardization. Compute the volume of thiosulfate solution which would be required for the titration of the smallest of the three standards on the assumption that the solution is exactly 0.1 N.

Now to the flask containing the smallest amount of copper standard add 10 ml. of the potassium iodide solution and allow to stand for only a few minutes. Run in the thiosulfate solution rapidly to within about 1 ml. of the calculated volume. This will also be indicated by the solution assuming a pale yellow color.

In order to secure the best possible end point add at this stage of the titration a drop of starch indicator and 10 ml. of potassium thiocyanate



reagent and shake the solution. This step is introduced to dislodge the adsorbed iodine from the cuprous iodide precipitate and results in a sharper end point.

Finally add 5 ml. of the starch solution and titrate to the end point by adding the thiosulfate solution dropwise. The end point is somewhat obscured by the presence of the precipitated  $\text{Cu}_2\text{I}_2$  but should be quite sharp, as marked by the disappearance of the blue color.

Treat another portion of standard copper solution with potassium acid phthalate and follow the same procedure as above. Do the same with the third portion.

From the data thus obtained here and in the comparison calculate the normalities of the sodium thiosulfate and iodine solutions. Calculate also the Cu titers of the two solutions.

**Determination of Copper in Copper Salts.** Weigh out three portions of the sample, as submitted, of about 0.5 gram each. If the samples are water soluble, dissolve each in about 50 ml. of water. If copper oxide samples are to be used, dissolve in a little nitric acid, heating if necessary. From this point the determination proceeds as with the standardization. Calculate the percentage of copper in the sample.

**Determination of Copper in Ores.** If the determination of copper is to be made on ores, minerals or other mixtures which contain oxidizing substances, the copper must first be freed from these interfering elements or modifications must be introduced to overcome these interferences. In the modification recently proposed by Park these interferences are overcome by the use of ammonium bifluoride and potassium acid phthalate.

Dry the sample at  $105^\circ\text{C}$ . for one hour.

Weigh out three 1-gram portions of the dried ore into 300 ml. beakers, add 10 ml. of concentrated nitric acid, cover with watch glasses, warm until the sample has practically gone into solution. Then rinse off the cover glasses and begin the evaporation on a water bath until fumes no longer are evolved.

Add a little more acid and digest until the sediment is white. Filter the solution into 250-ml. Erlenmeyer flasks and wash the residue and filter paper with weakly acidulated water until all copper color has been removed. Do not allow the solutions to exceed about 75 ml. in volume.

Treat the filtrate with 10 ml. of bromine water and boil. Cool and add dilute ammonium hydroxide until a precipitate begins to form.

Now add 2 grams of ammonium bifluoride. This reagent forms a complex ion,  $\text{FeF}_6^{3-}$ , with the ferric ion. Shake the flask until the brown precipitate dissolves.

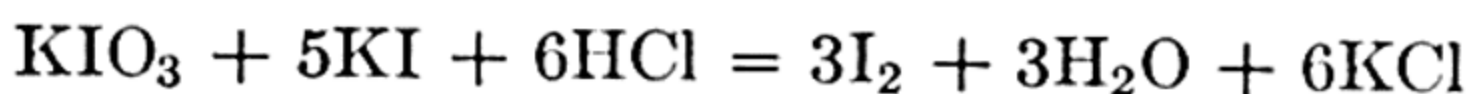
Finally add 1 gram of potassium acid phthalate.

From this point on the procedure is the same as that described on page 152 for the standardization.

When each sample in turn has been treated with the potassium iodide solution and titrated, calculate the percentage of copper in the sample.

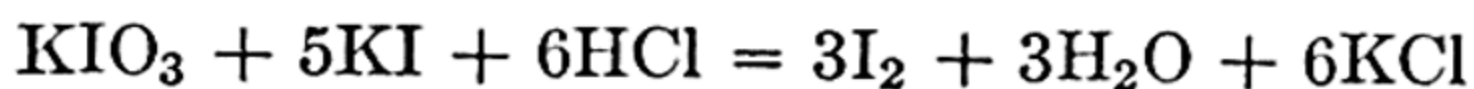
### IODATE AND BROMATE METHODS

Potassium iodate finds, as already indicated on page 143, extensive uses as an analytical reagent. Because it can be obtained in pure condition and consequently can be used directly as a primary standard, some chemists prefer it to iodine or certain other oxidizing agents. In fact, when it is in the same solution with potassium iodide and the solution is weakly acidified with HCl, iodine is liberated according to the equation

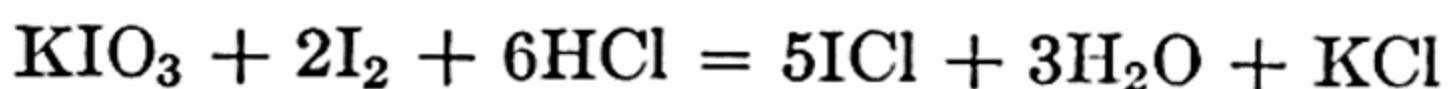


and the mixed reagent reacts like a solution of iodine itself. A convenient means of making a standard, normal solution of iodine is to weigh out the equivalent weight of pure  $\text{KIO}_3$ , add excess of KI and acidify when being used.

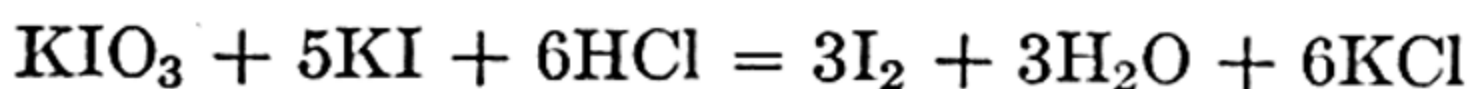
The use of  $\text{KIO}_3$  alone as a standard oxidizer without admixture of KI finds many applications. The conditions under which the titrations are carried out are here briefly described. In a strongly acid solution the final reduction product of  $\text{KIO}_3$  is iodine monochloride,  $\text{ICl}$ . When  $\text{KIO}_3$  reacts with reducing agents the intermediate product is  $\text{I}_2$ , which in turn reacts with the iodate to destroy the iodine. Titrations of this kind reach an end point when the color of the liberated iodine is discharged from a chloroform or carbon tetrachloride layer in the solution being titrated. The reactions by which  $\text{ICl}$  forms can be seen from the following, where KI is the reducing agent:



and



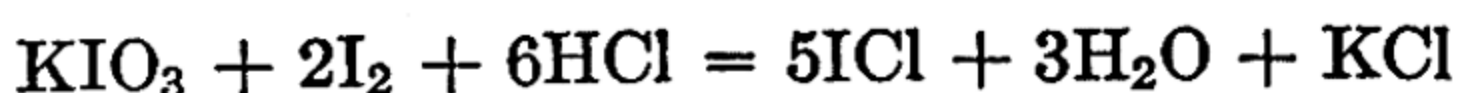
If the titration is stopped when the iodate has been reduced to iodine, which can be accomplished in solutions of low acidity, the liberated iodine can be titrated with standard thiosulfate. Thus iodides can be oxidized to free iodine by the reaction



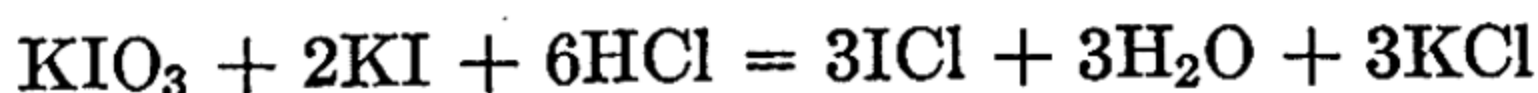
and determined in this way instead of effecting the formation of iodine monochloride.



From the equation

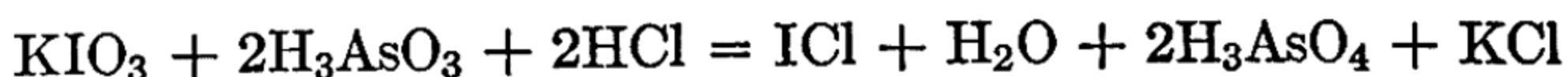


it is seen that iodine can be determined by direct titration with a standard solution of  $\text{KIO}_3$ . Likewise, iodides, such as  $\text{KI}$ , can be determined by a similar titration:

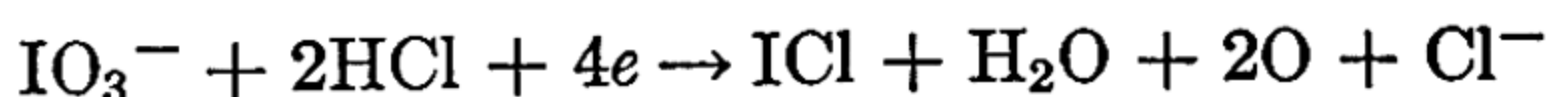


Among the many other substances that can be determined by titration with  $\text{KIO}_3$ , with the formation of iodine monochloride, are arsenites, sulfites, thiosulfates, persulfates, tin, antimony and copper thiocyanate.

In the reaction for the determination of arsenites according to the equation

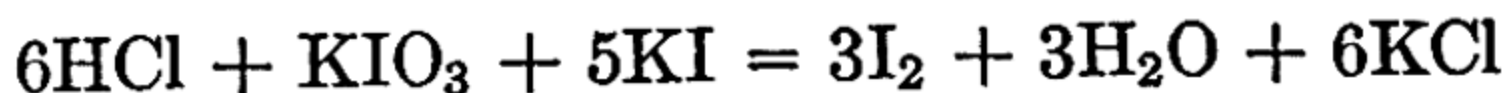


the change of  $\text{IO}_3^-$  to  $\text{ICl}$  is shown by the equation



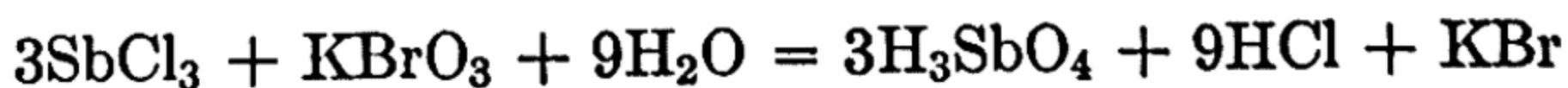
From this it is seen that, under these conditions, the equivalent weight of  $\text{KIO}_3$  is  $\text{KIO}_3/4$  or one-fourth the gram-molecular weight.

Certain substances, moreover, can be determined by use of a mixture of potassium iodate and potassium iodide, which react to liberate iodine. The iodine, in turn, can then be titrated with thiosulfate. The reaction just given for the determination of iodides

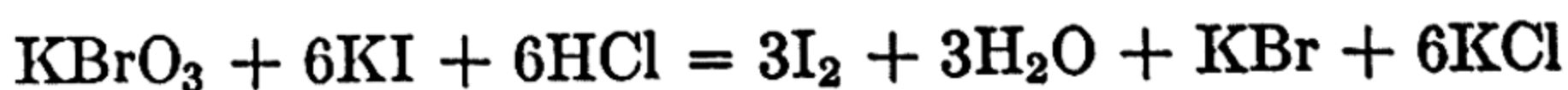


may be used, as well, for the determination of strong acids like  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  and, by special adaptation, for  $\text{H}_3\text{BO}_3$  and certain hydrolyzable salts.

Standardized solutions of potassium bromate,  $\text{KBrO}_3$ , are frequently used in the determination of many substances. This oxidizing agent may be used either alone or along with  $\text{KBr}$  or  $\text{KI}$  in a variety of ways. The titration may be stopped either when the bromate has been reduced to bromide or reduced to free bromine. As example of the first mode of procedure, the determination of such substances as the elements tin, iron, arsenic, titanium and antimony may be cited. In the case of antimony, the reaction proceeds in the following way:



The reaction of  $\text{KBrO}_3$  with iodides in an acid solution is an important one:



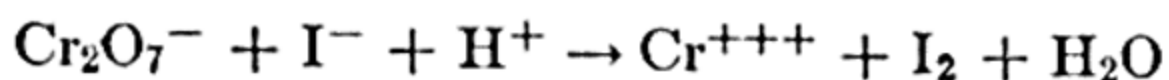
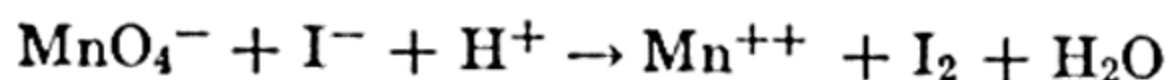
and furnishes still another method for the determination of iodides.

## QUESTIONS

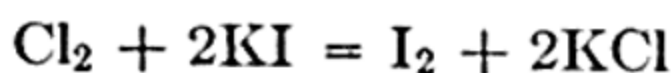
1. Show how the amount of iodine and sodium thiosulfate required for a liter of normal solution is calculated.

2. Write reactions which represent the standardization of sodium thiosulfate against (a) pure, resublimed iodine; (b) pure copper; (c)  $\text{KBrO}_3$ .

3. Suppose you had on hand a standard solution of  $\text{KMnO}_4$  or of  $\text{K}_2\text{Cr}_2\text{O}_7$ . How could you use either of these solutions for the standardization of a thiosulfate solution? Balance the following equations:



4. How is the following reaction:



applied (a) in qualitative analysis, (b) in quantitative analysis?

5. Outline an iodimetric and a permanganate method for the determination of hydrogen peroxide.

6. Outline an iodimetric and a permanganate method for the analysis of pyrolusite ( $\text{MnO}_2$ ).

7. How could you proceed with the determination of copper if ferric iron were also present in the sample?

## PROBLEM SET 9

## CALCULATIONS INVOLVING THE LIBERATION OF IODINE

1. What are (a) the  $\text{As}_2\text{O}_3$ , (b) the As, (c) the S and (d) the Cu titers of a 0.1 *N* iodine solution?

*Ans.* (a) 0.004946

(b) 0.003746

(c) 0.003206

(d) 0.006357

2. Find the normalities of solutions having the following titers:

(a) Cu titer = 0.006475

(b) S titer = 0.003820

(c) Cr titer = 0.001800

(d)  $\text{H}_2\text{SO}_3$  titer = 0.004022

3. A student standardized a sodium thiosulfate solution, obtaining the following data:

$$33.85 \text{ ml. I}_2 \approx 35.48 \text{ ml. Na}_2\text{S}_2\text{O}_3$$

After a proper treatment of the sample he found that 0.2202 gram of electrolytic copper required 38.12 ml. of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution and 2.24 ml. of the  $\text{I}_2$  solution for back-titration. Find the normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{I}_2$  solutions.

*Ans.* 0.0968 *N*; 0.1014 *N*

4. A  $\text{Na}_2\text{S}_2\text{O}_3$  solution was found to have a normality of 0.1024. If it is desired that each milliliter of this solution should be equivalent to 0.006357 gram of copper, to what volume should a liter of this solution be diluted?



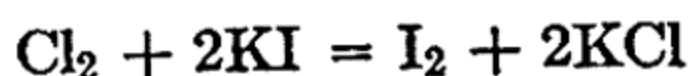
5. What normality should a  $\text{Na}_2\text{S}_2\text{O}_3$  solution possess if each milliliter is to represent 1 per cent of copper in 0.2000-gram samples. *Ans.* 0.03146 *N*

6. A 0.2984-gram sample of copper ore required 33.79 ml. of 0.0909 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  to titrate the iodine liberated from KI by the copper. Find the percentage of copper in the ore.

7. A  $\text{Na}_2\text{S}_2\text{O}_3$  solution was standardized with a  $\text{KMnO}_4$  solution by titration of the  $\text{I}_2$  liberated from KI by the  $\text{KMnO}_4$ . To a solution containing KI, 32.25 ml. of 0.1021 *N*  $\text{KMnO}_4$  were added. Find the normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  if 30.34 ml. were necessary for titration of the liberated iodine. *Ans.* 0.1085 *N*

8. A sample of lead paint was dissolved, the lead precipitated as  $\text{PbCrO}_4$  and this dissolved in acid. To the acid solution KI was added and the liberated iodine was titrated with 35.65 ml. of 0.1010 *N*  $\text{Na}_2\text{S}_2\text{O}_3$ . Find the weight of lead in the paint.

9. It is possible to determine the amount of free chlorine in swimming pool water by testing its action on KI:



and by titrating the liberated iodine with a standard thiosulfate solution. If a 100.00-ml. sample when treated with KI and titrated with 0.0102 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  required 6.75 ml., what was the concentration of  $\text{Cl}_2$  in the water in terms of parts per million by weight? *Ans.* 244 parts per million

10. A student's  $\text{Na}_2\text{S}_2\text{O}_3$  solution had been standardized with a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and the  $\text{Na}_2\text{S}_2\text{O}_3$  solution was then used in the analysis of a copper ore; 36.69 ml. of a 0.1 *N*  $\text{K}_2\text{Cr}_2\text{O}_7$  solution were allowed to react with an excess of KI and the liberated iodine was titrated with 34.92 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$ . The 0.2109-gram sample required 22.50 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  to react with the iodine liberated from KI by the dissolved sample. Find the percentage of copper in the sample.

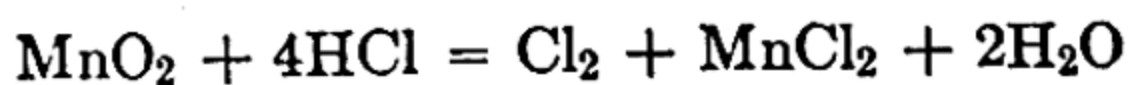
11. A portion of a mixture of  $\text{KBrO}_3$  and KI was treated with HCl and the  $\text{I}_2$  liberated in the reaction



was titrated with 34.73 ml. of 0.1000 *N*  $\text{Na}_2\text{S}_2\text{O}_3$ . Find the weight of  $\text{KBrO}_3$  in the sample taken for analysis. *Ans.* 0.0967 gram

12. If 1.00 ml. of  $\text{KMnO}_4$  solution can liberate 0.1527 gram of iodine from KI, what weight of pure  $\text{MnO}_2$  can be reduced by the same volume of oxalic acid as is oxidized by 32.20 ml. of the above permanganate solution?

13. A sample of  $\text{MnO}_2$  ore was treated with HCl, liberating chlorine:



and the chlorine passed into a solution containing excess KI:

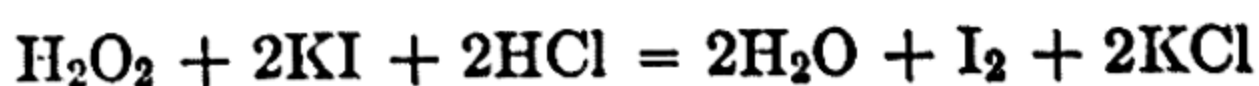


The iodine was titrated with a 0.1250 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  solution requiring 38.55 ml. for a 0.4850-gram sample of the ore. Calculate the percentage of  $\text{MnO}_2$  in the ore.

*Ans.* 43.20 per cent

14. What weight of potassium iodate will liberate sufficient iodine to react with 35.25 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  having an arsenious oxide titer of 0.04530? (Reaction similar to that in Problem 11.)

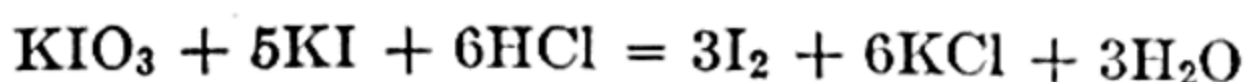
15. Hydrogen peroxide may be determined by an iodometric method as shown by the following reaction:



If a 10-ml. sample of  $\text{H}_2\text{O}_2$  (sp. gr. 1.01) requires 30.30 ml. of 0.5000  $N$   $\text{Na}_2\text{S}_2\text{O}_3$  for reaction with the liberated iodine, what is the percentage of  $\text{H}_2\text{O}_2$  in the sample?

*Ans.* 2.55 per cent

16. From the reaction



calculate the gram-equivalent weight of  $\text{KIO}_3$ .

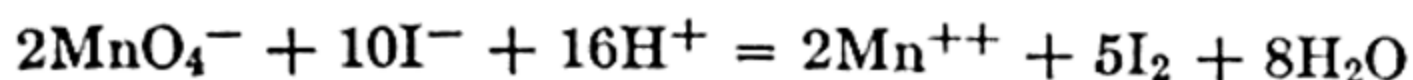
17. How many grams of (a)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , (b)  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and (c)  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  must be used to make a liter of each of these reagents, each equivalent to a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution of which 1 ml. can liberate 0.01268 gram of iodine from KI?

*Ans.* (a) 27.80

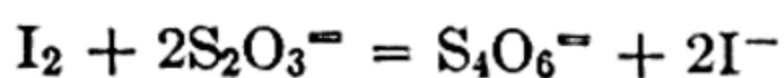
(b) 6.30

(c) 24.82

18. A  $\text{Na}_2\text{S}_2\text{O}_3$  solution was standardized by means of a previously standardized solution of  $\text{KMnO}_4$ , basing the method on the reactions:



and

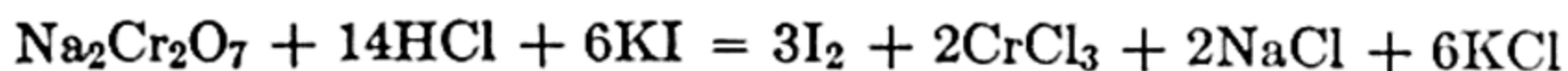


Using the following data, calculate the strength of the thiosulfate solution:  $\text{KMnO}_4$  used, 35.00 ml.;  $\text{Na}_2\text{S}_2\text{O}_3$  used, 38.72 ml.; strength of  $\text{KMnO}_4$ , 0.1260  $N$ .

19. How much iodine will be liberated from 35.67 ml. of a 0.1482  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution when treated with KI and HCl?

*Ans.* 0.6703 gram

20. A sample of chromium ore was oxidized to  $\text{Na}_2\text{CrO}_4$  by a sodium peroxide fusion, and this, after removal of iron and other impurities, was treated with HCl to convert it into  $\text{Na}_2\text{Cr}_2\text{O}_7$ . An excess of KI was then added, liberating iodine in accordance with the reaction



The liberated iodine was titrated with 38.65 ml. of a 0.1000  $N$  solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . If the weight of sample was 1.2230 grams what was the percentage of chromium in the sample?

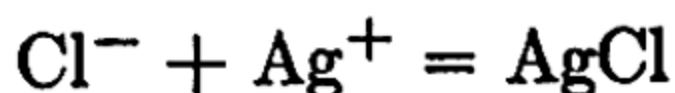


## CHAPTER V

### VOLUMETRIC PRECIPITATION METHODS

Precipitation methods depend upon the practically complete precipitation of a compound containing the element whose determination is undertaken. Volumetric precipitation methods differ from gravimetric precipitation methods in that, instead of filtering, purifying and weighing the precipitate, the amount of reagent required to complete the reaction is carefully measured, the completion of the reaction being indicated by a sharp change in color of an indicator or by use of electrical instruments as in potentiometric titration. The fundamental requirements for all volumetric precipitation processes are (1) a precipitation reaction which goes to practical completion, (2) a standardized solution of a precipitating reagent and (3) a means of indicating the end point. The third condition, namely, a means of indicating the end point, is the hardest requirement to fulfill, and it may be said that in general many precipitation reactions might be adapted to the volumetric technique if it were not for the lack of suitable indicators. Indicators, which must show a pronounced change in color immediately upon completion of the main reaction, are comparatively hard to find, and determinations for which such indicators are available are few in number. Some examples are considered below.

**Typical Precipitation Methods.** Chlorides, bromides and iodides can be accurately determined by titration with a standard silver nitrate solution. For chlorides, the reaction is



Reactions analogous to the above take place with the bromide and the iodide ion. The process may be reversed for the determination of silver by use of a standard solution of sodium chloride.

In the method of Mohr, for the determination of chlorides, the indicator is potassium chromate, which reacts with silver nitrate to form a deep red precipitate of  $\text{Ag}_2\text{CrO}_4$  when a drop of the standard  $\text{AgNO}_3$  beyond the equivalent volume has been added to the chloride solution. In the procedure given for chlorides in the following section, an adsorption indicator, dichlorofluorescein, is utilized.

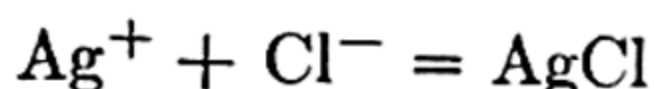
A fairly satisfactory method for zinc is based on the reaction between zinc and potassium ferrocyanide, giving a precipitate of the approximate composition  $K_2Zn_3(Fe(CN)_6)_2$ , uranyl acetate being used as indicator. Lead may be determined volumetrically by use of a standard potassium chromate solution, tannin being used as indicator.

The determination of silver by titration with a standard solution of potassium thiocyanate, according to the method of Volhard, is another typical example of a volumetric precipitation procedure, the procedure being given in detail later in this chapter.

### THEORY OF VOLUMETRIC PRECIPITATION

**Equilibria in Volumetric Precipitation Reactions.** The chief application of the Law of Chemical Equilibrium to precipitation reactions concerns the Solubility Product Principle. This principle states that, in a solution in which a precipitate has formed, the product of the gram-ion concentrations of the ions in the saturated solution surrounding the solid is always equal to a constant, called the solubility product constant. In order for a solution to become saturated with respect to the ions which enter into the chemical composition of the precipitate, enough ions of the precipitating agent must be supplied so that their concentration, multiplied by the concentration of the ion whose precipitation is sought, exactly equals the numerical value of the constant for the precipitate in question. For the precipitate actually to form the constant must be exceeded.

In simple cases such as the precipitation of  $AgCl$  by the ionic reaction

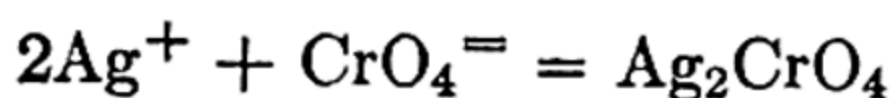


the solubility product equation takes the form:

$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.}$$

in which  $C_{Ag^+}$  and  $C_{Cl^-}$  are the concentrations (gram-ion quantities referred to a liter) of  $Ag^+$  ion and  $Cl^-$  ion in equilibrium with each other, and  $K_{s.p.}$  is the solubility product constant of  $AgCl$ .

In more complicated cases, such as the formation of  $Ag_2CrO_4$ , in the reaction



the equation is

$$(C_{Ag^+})^2 \times C_{CrO_4^{2-}} = K_{s.p.(Ag_2CrO_4)}$$

Solubility product constants are usually calculated from solubility data, and a table of such values is given on page 182. A liter of water, at room temperature, will dissolve approximately 0.00001 of a gram-



molecular weight of AgCl; the saturated solution is  $1 \times 10^{-5}$  molar with respect to the dissolved salt. In such a solution the concentration of  $\text{Ag}^+$  ions is  $1 \times 10^{-5}$  gram-ion, and the concentration of  $\text{Cl}^-$  ions is also  $1 \times 10^{-5}$ . The solubility product equation is therefore

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{\text{s.p.}}$$
$$10^{-5} \times 10^{-5} = 1 \times 10^{-10}$$

Although in this particular solution, which was formed by the dissolving of AgCl, the concentrations of each set of ions are equal, such need not always be the case in order for equilibrium to be reached. Since the constant is a product of two factors, these may be varied at will. Thus in order to reach equilibrium and shortly thereafter to have a precipitate form, in a solution which contains a chloride-ion concentration of, say,  $10^{-2}$ , a concentration of  $\text{Ag}^+$  ions of  $10^{-8}$  would be required for saturation and equilibrium, and a slight quantity beyond this results in the formation of solid AgCl. Such equilibrium concentrations give the quantities required for the *initial* formation of the precipitate.

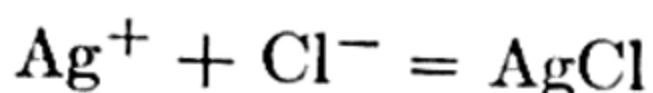
But in order to have quantitative (practically complete) precipitation, an amount of  $\text{Ag}^+$  must be added which is equivalent to the  $\text{Cl}^-$  present. This is the condition in a quantitative titration precipitation process. The titration must stop when an equivalent amount of precipitating agent is added, this amount being signified by the color change of the indicator. No advantage can be taken in volumetric precipitation processes of an excess of precipitating reagent. When an equivalent amount has been added, the concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  remaining in solution in equilibrium with the precipitated AgCl are equal and, in fact, are identical to those obtained by dissolving AgCl in water. When the titration is completed there remain, in a liter of solution,  $10^{-5}$  gram-ion of  $\text{Cl}^-$  and  $10^{-5}$  gram-ion of  $\text{Ag}^+$ . In 100 ml. the volume of the solution at the end of the titration, there would remain  $1 \times 10^{-6}$  gram-ion of unprecipitated chloride ion. This corresponds to  $1 \times 10^{-6} \times 35.46$  or about 0.00005 of a gram of chloride. Although this represents a loss and therefore an inherent error in the determination, the amount is less than that which can be determined by the apparatus used.

### VOLUMETRIC DETERMINATION OF CHLORIDES

There exist two general titration methods for the determination of chlorides, (1) the Volhard method, which employs standard solutions of silver nitrate and potassium thiocyanate, a modification of which is described later in the determination of silver, and (2) the Mohr method, which employs a standard solution of silver nitrate with potassium

chromate as indicator. A modification of the Mohr method introduced by Fajans utilizes an adsorption indicator and is here outlined. This gives practice with an example of these newly developed interesting indicators.

**Outline of Method.** The reaction which takes place is the simple ionic one leading to the formation of  $\text{AgCl}$



A solution of  $\text{AgNO}_3$ , approximately 0.1 N, is prepared and standardized with pure  $\text{NaCl}$ . The adsorption indicator is dichlorofluorescein, which produces a pink color due to the adsorption of  $\text{Ag}^+$  ions on the particles of  $\text{AgCl}$ . This color develops at the equivalence point in the titration.

#### PREPARATION AND STANDARDIZATION OF AN APPROXIMATELY 0.1 N $\text{AgNO}_3$ SOLUTION

A normal solution of  $\text{AgNO}_3$  should contain the gram-molecular weight of  $\text{AgNO}_3$  in a liter of solution, since the valence of Ag, the precipitation ion, is 1 and is directly equivalent to one hydrogen atom. To conserve this expensive chemical, prepare a half-liter of the solution by weighing 8.5 grams of  $\text{AgNO}_3$ , dissolving and making up to 500 ml.

Weigh accurately three portions of pure  $\text{NaCl}$  (previously carefully prepared and dried) of about 0.2 gram each, into three 250-ml. Erlenmeyer flasks. Dissolve each portion of the standard in 50 ml. of distilled water. To each add 8 to 10 drops of the dichlorofluorescein indicator and about 0.1 of a gram of dextrine, the latter for the purpose of dispersing the  $\text{AgCl}$  when precipitated. Titrate the solutions, with constant swirling, and out of contact of strong sunlight. The end point is reached when a pink color appears in the solution.

Calculate the Cl titer and the normality of the  $\text{AgNO}_3$  solution.

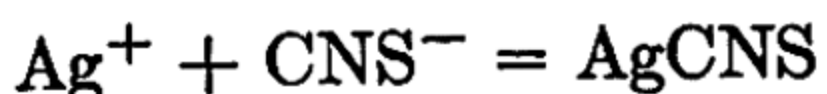
**Determination of Chloride in a Sample of Soluble Chloride.** **PROCEDURE.** Weigh out accurately about a 1-gram portion of the dried chloride sample. Dissolve in 50 ml. of distilled water and make up to 250 ml. in a volumetric flask. Pipet a 50-ml. aliquot portion, add the indicator and dextrine as in the standardization and titrate with the standard silver nitrate. Calculate the percentage of chloride in the sample.

*Note:* It is suggested that the same sample of soluble chloride be used in the gravimetric determination of chlorides (see page 191) and that results be compared for the two methods. Obviously, the instructor should withhold the true percentage of chloride in the sample until both reports have been submitted.

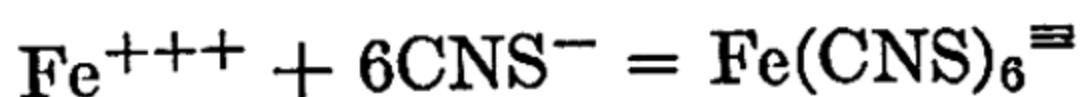


## VOLUMETRIC DETERMINATION OF SILVER

The method here outlined is that first proposed by Volhard and consists of titration of the dissolved silver by standard potassium thiocyanate, a ferric salt being used as the indicator. The fundamental reaction involved is



wherein the silver thiocyanate forms as a white precipitate. After (practically) all the silver has been precipitated the reaction between the ferric ions of the indicator solution and the thiocyanate ions sets in:



producing a complex ion which is red, thus furnishing the indication that the main reaction has run to completion.

The determination of silver by this method involves the preparation and standardization of a dilute solution of KCNS and the subsequent use of this standard solution in the titration of the silver samples.

#### PREPARATION AND STANDARDIZATION OF AN APPROXIMATELY 0.05 N KCNS SOLUTION

The solution of KCNS should be dilute, about 0.05 N. A normal solution of a precipitating reagent should, by definition, contain an equivalent weight of the precipitating ion per liter of solution, namely, that amount of ion which will replace or be equivalent to 1.008 grams of hydrogen. Since the valence of the anion,  $\text{CNS}^-$ , is 1, the molecular weight of the potassium salt, KCNS (97.17 grams), in a liter of solution constitutes a normal solution of this reagent. To make an exactly 0.05 N solution, 0.05 of the gram-molecular weight, that is,  $97.17 \times 0.05$  or 4.8585 grams, of the pure salt are required for a liter of solution or 2.4293 grams for 500 ml.

It is possible to procure or prepare KCNS of sufficient purity to serve as a primary standard, thus obviating the necessity of standardization by titration against pure  $\text{AgNO}_3$ . If pure KCNS is available, weigh out exactly 2.4293 grams of the pure salt, dissolve in a little distilled water, transfer to a 500-ml. volumetric flask and fill to the mark with distilled water. The following procedure provides for standardization with pure  $\text{AgNO}_3$  in case pure KCNS is not supplied.

**Procedure for Standardization.** Procure from the supply room or from the instructor the following supplies: 1 gram of  $\text{AgNO}_3$ , 2.5 grams of KCNS and 10 grams of ferric alum.

Grind the  $\text{AgNO}_3$  crystals in a mortar, place the powder on a watch glass, cover it with a clean sheet of filter paper and place in a drying

oven at 105–110°C. for about one-half hour. In the meantime, weigh out about 2.5 grams of KCNS and dissolve it in a small amount of distilled water. Transfer the solution to a 500-ml. measuring flask and dilute to the mark. Pour the solution into a clean liter bottle. This solution is approximately 0.05 normal.

Prepare the ferric alum indicator solution by saturating 30 ml. of distilled water with ferric alum and adding enough  $\text{HNO}_3$  (sp. gr. 1.20) to impart a faint yellow color to the solution.

The weight of  $\text{AgNO}_3$  to be taken for standardizing the KCNS solution can be determined by a simple calculation. Assume that the KCNS solution is exactly 0.05 normal and that 35 ml. will be used for one standardization titration. A liter of normal thiocyanate solution will react with 169.89 grams of silver nitrate; a liter of 0.05 normal solution will therefore react with  $0.05 \times 169.89$  or 8.4945 grams, and 1 ml. of a solution of this normality will bring into reaction 0.008494 gram of silver nitrate. Since 35 ml. are assumed for the titration, the weight of  $\text{AgNO}_3$  required is  $35 \times 0.008494$  or 0.2973 gram.

Weigh out accurately three portions of the dried  $\text{AgNO}_3$  of about 0.3 gram each, and transfer them to 200-ml. beakers. Dissolve each in about 50 ml. of distilled water and add 10 ml. of dilute, freshly boiled  $\text{HNO}_3$  (sp. gr. 1.20) and 5 ml. of the ferric alum indicator.

Rinse out a buret with a small amount of the KCNS solution, and fill the buret to the top of the graduations. Take the buret reading, place one of the silver nitrate solutions under the buret and run in the thiocyanate solution slowly with constant stirring. Let the precipitate settle at intervals, and watch for a change in the color of the supernatant liquid. When the first pink tinge appears which lasts for at least one minute take the final buret reading. Repeat with the other two solutions, but run these to 2 ml. of the end point, found by calculating from the result of the first run the probable volume of solution required, and then slowly titrate to the end point.

If the results as calculated below do not agree to within 2 parts per 1000, make another set of determinations.

From the number of milliliters of KCNS solution and the number of grams of  $\text{AgNO}_3$  used in each case calculate the Ag titer of the KCNS solution; also, calculate the normality of the KCNS solution. Record the titers and the normalities and average each set.

#### DETERMINATION OF SILVER IN SILVER ALLOYS

Samples of silver alloy, not exceeding 70 per cent of copper, are weighed out and dissolved in nitric acid. The solutions are boiled, cooled, diluted, and ferric alum indicator is added, after which they are



titrated with standard KCNS solution. Copper in the alloy, if present in too high a concentration, will obscure the end point. The purpose of boiling the solution is to expel lower oxides of nitrogen which tend to give a red color to the solution and consequently a false end point.

**Procedure.** Weigh out three separate samples of the alloy of about 0.3 gram each, and place in beakers of 200-ml. capacity. Dissolve each sample in 15 ml. of dilute, freshly boiled  $\text{HNO}_3$  (sp. gr. 1.20), heating gently. If the samples do not dissolve readily, add more  $\text{HNO}_3$ .

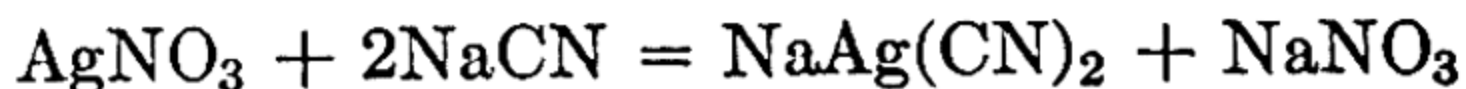
Cool, dilute to 50 ml. with distilled water, add 5 ml. of the indicator solution and titrate with KCNS solution, following the same procedure used in standardization. If results do not check, repeat the determination.

From the volume of KCNS solution used and the strength of the thiocyanate solution calculate the weight of silver in the sample. Report the results as "fineness," that is, parts of silver per thousand.

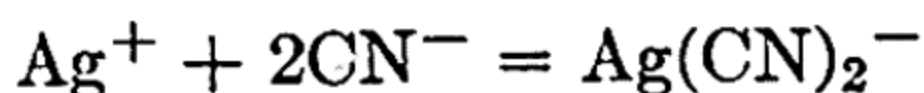
#### METHODS IN WHICH COMPLEX IONS ARE FORMED

Closely allied with the simple precipitation methods and included in the same classification are those in which a complex salt is formed. Important among these is the determination of cyanides or, conversely, silver, as well as the use of a standard KCN solution in the determination of nickel and copper.

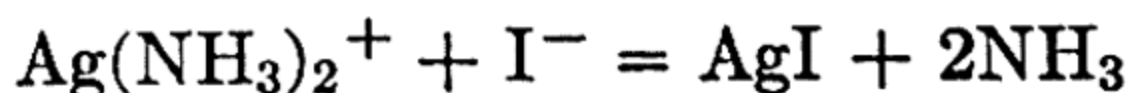
In a cyanide determination the reaction is



or ionically



and when an excess of standard silver nitrate is added, a precipitate of silver cyanide forms. The end point is obtained by adding a mixture of  $\text{NH}_4\text{OH}$  and  $\text{KI}$ . The  $\text{NH}_4\text{OH}$  prevents  $\text{AgCN}$  from precipitating owing to the formation of  $\text{Ag}(\text{NH}_3)_2^+$  ions but  $\text{AgI}$  is formed instead by the reaction



When a yellowish opalescence of  $\text{AgI}$  appears, the end point is reached.

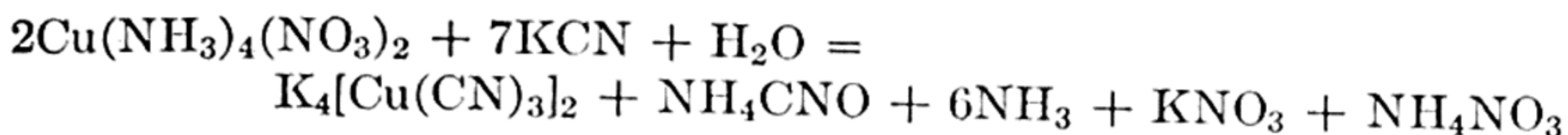
The determination of nickel by the cyanide titration is frequently used in alloy and steel analysis. The main reaction is the formation of complex nickel cyanide ions.



The indicator, as in the method for cyanides, is  $\text{AgI}$ , produced by adding

KI and  $\text{AgNO}_3$  to the reaction mixture, but the end point is marked by the disappearance rather than the formation of an opalescence.

A method for copper sometimes employed consists in titrating an ammoniacal copper solution with standard KCN, the reaction being expressed by the equation



The end point is the disappearance of the blue color of the ammonia-copper complex ion.

### QUESTIONS

1. Give equations for the reactions involved in the most important volumetric precipitation procedures. Why are there so few such methods?
2. What indicator or indicators would you employ for the determination of (a) halides, (b) silver, (c) lead, (d) cyanides, (e) zinc?
3. Explain the action of an adsorption indicator.
4. Suggest a method for standardizing a hydrochloric acid solution using (a) Mohr's method, (b) Fajans' method.
5. Outline a method for the determination of soluble thiocyanates. Can a standard solution of KCNS be made without standardization?
6. For use in volumetric precipitation methods what pure substances could you use for standardizing (a) silver nitrate, (b) sodium chloride, (c) potassium thiocyanate?
7. Show how the equivalent weight of precipitating ions is related to the equivalent weight for hydrogen.
8. Write ionic reactions for the cyanide determination of (a) copper, (b) nickel, (c) silver.

### PROBLEM SET 10

#### VOLUMETRIC PRECIPITATION

1. How many grams of sodium chloride must be taken to prepare 1000 ml. of a solution which will be equivalent to 10 milligrams of Ag per milliliter?

*Ans.* 54.1 grams

2. A solution of  $\text{AgNO}_3$  is known to contain 21.857 grams of  $\text{AgNO}_3$  per liter. Calculate the following titers.

- (a) Cl titer
- (b) Br titer
- (c) KCN titer
- (d)  $\text{CNS}^-$  titer

3. What quantity of pure NaCl should be weighed out so that not more than 35 ml. of 0.100 N  $\text{AgNO}_3$  will be used in a standardization?

*Ans.* 0.205 gram

4. Calculate (a) the KCNS titer and (b) the Cl titer of a 0.1286 N solution of  $\text{AgNO}_3$ .

5. Find the percentage of NaCl in a sample of rock salt, a 0.2600-gram sample of which required 42.25 ml. of 0.1000 N  $\text{AgNO}_3$  for the precipitation of the chloride.

*Ans.* 95.00 per cent



6. What weight of pure  $\text{AgNO}_3$  should be taken for the standardization of an approximately 0.08000  $N$  solution of  $\text{KCNS}$  if not more than 40.00 ml. of the solution is to be used?

7. If 32.75 ml. of a  $\text{KCNS}$  solution, the normality of which is 0.04782, react with 34.62 ml. of a  $\text{AgNO}_3$  solution, what is the normality of the latter?

*Ans.* 0.04523  $N$

8. Calculate the percentage of silver in an alloy, 0.2980 gram of which required 38.95 ml. of a 0.05125  $N$   $\text{KCNS}$  solution.

9. If a certain  $\text{KCNS}$  solution has a  $\text{Ag}$  titer of 0.01078, what is its normality? How much silver can be precipitated by 25.00 ml. of this solution?

*Ans.* 0.1000  $N$ ; 0.2685 gram

10. How many grams of pure  $\text{AgNO}_3$  are required for the precipitation of the  $\text{CNS}$  in 25.00 ml. of 0.05000  $N$   $\text{KCNS}$  solution?

11. If the lead in a sample of alloy is to be precipitated as  $\text{PbCrO}_4$ , what volume of 0.1000  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  will be required for a 0.5000-gram sample which contains 30 per cent  $\text{Pb}$ ?

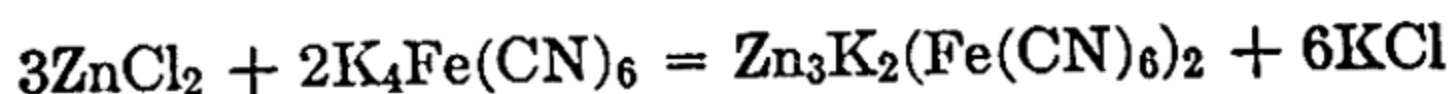
*Ans.* 14.49 ml.

12. Calculate the error made in terms of unprecipitated  $\text{Cl}^-$  in a volumetric determination of chlorides by titration with standard  $\text{AgNO}_3$ , if the total volume of solution after titration is 100 ml. The  $K_{s.p.}$  of  $\text{AgCl}$  is  $1.1 \times 10^{-10}$ .

13. What volume of 0.1020  $N$   $\text{BaCl}_2$  is required to precipitate the sulfate from a 0.2300-gram sample of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  which is 85.00 per cent pure?

*Ans.* 14.6 ml.

14. Zinc ores may be analyzed by dissolving the ore, separating the zinc and titrating it with a standard potassium ferrocyanide solution according to the reaction



Find the percentage of zinc in an ore, 0.5026 gram of which required 26.25 ml. of 0.1500  $N$  ferrocyanide solution.

15. How many grams of  $\text{K}_2\text{CrO}_4$  must be taken to make a liter of 0.1000  $N$  solution to be used for the precipitation of lead as  $\text{PbCrO}_4$ ? What is the  $\text{Pb}$  titer of a 0.5213  $N$  solution of  $\text{K}_2\text{CrO}_4$ ?

*Ans.* 9.711 grams; 0.05401

16. To a 0.2652-gram sample of a mixture of pure  $\text{NaCl}$  and  $\text{KCl}$  were added 41.00 ml. of 0.1  $N$   $\text{AgNO}_3$ . After precipitation of the chlorides as  $\text{AgCl}$ , the excess of  $\text{AgNO}_3$  was titrated with 3.85 ml. of 0.1  $N$   $\text{KCNS}$ . What was the weight of  $\text{KCl}$  in the mixture?

17. A 0.4895-gram sample of a phosphate was precipitated as  $\text{Ag}_3\text{PO}_4$ . The silver phosphate was dissolved in  $\text{HNO}_3$  and the silver titrated with 38.60 ml. of a 0.05000  $N$   $\text{KCNS}$  solution. Calculate the percentage of  $\text{PO}_4$  in the sample.

*Ans.* 12.50 per cent

18. A 0.6324-gram sample of a material containing iodides was treated with 50.00 ml. of a 0.1000  $N$  solution of  $\text{AgNO}_3$ , the precipitated  $\text{AgI}$  filtered off and the excess  $\text{AgNO}_3$  titrated with 20.00 ml. of 0.05000  $N$   $\text{KCNS}$ . Calculate the percentage of iodide present.

19. Soluble cyanides may be determined by volumetric precipitation with standard silver nitrate. If a 0.2000-gram sample requires 25.25 ml. of 0.05000  $N$   $\text{AgNO}_3$ , what is the percentage of  $\text{KCN}$  in the sample?

*Ans.* 41.2 per cent

20. It is desirable that the volumes of a 0.05  $N$  solution of  $\text{NaCl}$  used for titrating samples of silver alloy should range between 25 and 40 ml. What weights of alloy should be taken for analysis if the samples are thought to contain approximately (a) 25 per cent; (b) 50 per cent; (c) 75 per cent; (d) 95 per cent?

*PART III*  
*GRAVIMETRIC ANALYSIS*

CHAPTER VI

**THE THEORY, TECHNIQUE AND CALCULATIONS  
OF GRAVIMETRIC PRECIPITATION METHODS**

Gravimetric methods of analysis are those in which the desired constituent is separated and weighed in the form of a pure compound or a pure metal or in which a volatile product is evolved. These methods are therefore classified into (1) gravimetric precipitation methods; (2) evolution methods; (3) electrolytic precipitation methods. The technique differs widely for these three types of methods. The gravimetric precipitation methods are by far the most important and numerous.

All gravimetric precipitation methods are based on reactions in which a precipitate is produced through the action of a chemical precipitating agent. The precipitate thus obtained, which must contain all of the desired constituent, must be quantitatively separated from the solution, carefully purified, dried or converted into another compound whose chemical composition is definite and known and then finally weighed. Certain definite conditions must be fulfilled and certain requirements met in order that the selected reaction may become an accurate quantitative method of determination. These fundamental conditions and the manner of satisfying them are discussed below.

**FUNDAMENTAL REQUIREMENTS OF GRAVIMETRIC  
PRECIPITATION METHODS**

Reactions which take place because a precipitate forms do not necessarily run far enough to completion to make the reaction quantitative. Furthermore, the precipitated compound may not be in the condition, either chemically or physically, necessary for conversion and weighing in the form of a pure compound of definite, known composition. Gravimetric methods which give the accuracy demanded in exact chemical analysis must meet the following requirements.



1. The reaction must run practically to completion.
2. The precipitate formed must be practically insoluble in the medium in which it is precipitated and must contain (practically) all of the desired constituent. Furthermore, it must not contain any undesired constituent.
3. The physical condition of the precipitate must be such that it can be readily filtered and washed free of impurities.
4. The precipitate must be capable of being dried or ignited to a pure form, of definite and known composition.

It is evident that, if the nature of the reaction or of the precipitate is such that any one of the above conditions is not satisfactorily fulfilled, the method will be inaccurate and, if fulfilment is seriously lacking in any respect, the reaction cannot be used as a quantitative method. A consideration of these essential conditions will make it clear why reactions must be chosen with care and why the operations attendant upon carrying out the process must be executed with the best possible technique. It should be the aim of the student, in carrying out the following representative procedures, to subject each method to a thorough criticism with respect to these requirements.

**Completeness of Reaction.** This first condition is self-evident, since the desired constituent is to be isolated and eventually weighed. No reaction runs absolutely to completion, since an equilibrium is reached in every reaction. However, the important condition here is that the reaction should run as near to completion as possible. Many reactions in which relatively insoluble precipitates are formed are among those which do go, for all practical purposes, to completion.

**Insolubility of the Precipitate.** This second condition can be regarded as a corollary of the first, because the mechanism by which these reactions run to practical completion is by the separation of an insoluble product. The equilibrium condition which determines the extent to which precipitation takes place is a direct application of the law of chemical equilibrium, and is embodied under the Solubility Product Principle. Its application to quantitative precipitation is of considerable importance and is discussed in more detail in a following section.

The precipitate must contain (practically) all of the desired constituent. Chemically it must be a compound which contains the ion whose determination is undertaken. It is not essential that the compound as precipitated be chemically pure or even have a definite chemical composition while being precipitated. It is true that many precipitates do have a definite composition, but some do not and all are more or less contaminated with absorbed precipitating agent, with salts of other



constituents which may be in the solution and with varying amounts of adsorbed water or water of hydration. Thorough washing and drying or ignition are necessary to convert the precipitate into a compound of unquestioned definite composition.

**Physical Characteristics of the Precipitate.** The physical nature of the precipitated compound is as essential a condition as completeness of precipitation, for if the precipitate cannot be filtered easily and washed free of impurities, it is useless for the purposes of gravimetric analysis. The ideal characteristic of a precipitate is a coarsely crystalline state, in which condition filtration and washing are most easily accomplished. Certain precipitates, however, are gelatinous and certain others finely divided, two conditions which are undesirable in handling gravimetric determinations.

Finely divided and gelatinous substances tend to assume the colloidal state. A colloid is matter in a finely divided condition, the particles being so small that they cannot be separated from the solution by ordinary filtration methods. Colloids will not settle, will pass through the pores of filter paper or, if of a slimy nature, will clog the pores of the filter. These objectionable properties of colloidal precipitates, together with the fact that colloidal particles adsorb ions and salts on their surfaces, introduce difficulties in the filtration and washing of certain precipitates.

Adsorption of dissolved salts by finely divided and gelatinous precipitates is especially objectionable, because the adsorbed material is extremely hard to remove and thus contaminates the precipitate and renders impossible its conversion into a pure compound. In certain cases this contamination can be minimized by slow precipitation, by digestion and by repeated washing, but if these remedies fail the method will not give accurate results and must be discarded.

**Definiteness of Chemical Composition.** The precipitate must be freed from impurities by washing and filtration, and then dried or ignited to a form whose chemical composition is known, before it is finally weighed. This is evident from the fact that if the weight and formula are known, and the weighed compound carries all of the desired constituent and nothing else, the amount present in the sample can be calculated by directly applying the Law of Definite Composition.

## THE TECHNIQUE OF GRAVIMETRIC ANALYSIS

The successful fulfilment of the fundamental requirements of gravimetric precipitation processes depends very largely on the manner in which the experimental steps are carried out. The steps involved in



every determination of this kind are, in order: (1) securing a representative sample, (2) weighing a suitable amount of sample, (3) dissolving the sample, (4) precipitating the desired constituent, (5) filtering and washing the precipitate, (6) drying or igniting the compound and, finally, (7) cooling and weighing the product.

Sampling has already been considered in Chapter I. As in volumetric determinations, student samples are usually issued in uniform condition and require, in some instances, only drying.

**Weighing the Sample.** The proper weight of sample to be taken for an analysis must be decided upon for each type of material. The rule which governs this is: Enough sample should be taken to give sufficient precipitate so that the dried or ignited product can be accurately weighed and the analysis conveniently carried out with a single set of apparatus but not so much that the operations of filtering, washing and drying consume too much time. The amount of sample to take is determined by the content of the constituent sought. If the constituent is suspected of being present in small amount a relatively larger sample must be taken; on the other hand, if the sample is thought to contain large amounts, a smaller portion of sample should be taken. The approximate content in the sample, if not known, is usually determined by a well-conducted qualitative analysis. In the case of students' samples the procedures provide for the proper weight to be taken.

**Dissolving the Sample.** Water-soluble samples ordinarily will present no difficulty in dissolving. In some cases the water must be acidified. Dilute nitric acid is the usual solvent for water-insoluble samples, but in some cases dilute hydrochloric acid is preferable. In no case should the solvent exceed 100 ml., for it must be remembered that the larger the volume of resulting solution, together with the wash reagent which later must be used, the greater will be the loss of precipitate. The solution should always be kept as small as possible.

Materials which resist acid treatment must be fused to get them into solution. The commonest flux for materials of an acid nature, such as silicates, is  $\text{Na}_2\text{CO}_3$ . For basic materials an acid flux such as  $\text{KHSO}_4$  is usually used.

**Precipitation.** The chief concern in precipitation is so to arrange details, whenever possible, as to favor the production of large-grained crystals, since, as we have seen, precipitates that are finely divided or gelatinous are too hard to filter and wash. Slow, dropwise addition of precipitating agent, precipitation in warm solutions and digestion, i.e., heating the solution with its precipitate to nearly boiling for some time, all favor the formation of good precipitates. Stirring during precipitation is to be recommended.

Tests for complete precipitation must always be made by noting whether or not a precipitate or turbid solution results on adding an additional portion of the precipitating reagent to the clear, supernatant solution or to the filtrate.

**Washing and Filtering.** Impurities adsorbed or mechanically entrained in the precipitate must be washed out as completely as possible. Washing by decantation, in which the precipitate is allowed to settle and the supernatant liquid poured off through the filter, is always to be preferred. Several successive, small portions of the wash water should be used, stirring after each addition and, after the precipitate has settled, pouring off the solution through the filtering medium. The precipitate is then transferred to the filter paper or Gooch crucible by tip-

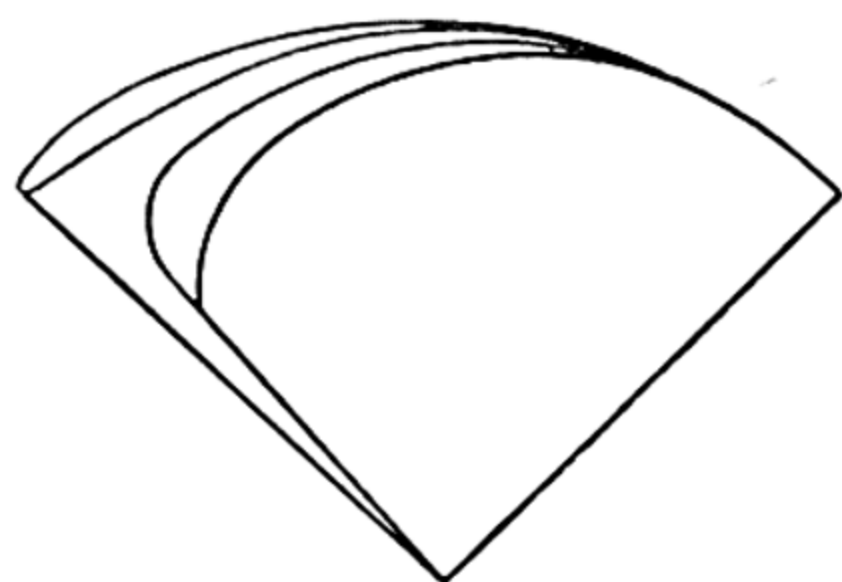


FIG. 12. Folded filter paper.

ping the beaker, holding a stirring rod against the lip of the beaker, as shown in Fig. 13, and directing a stream of water from the wash bottle into the bottom of the inverted beaker. Particles adhering to the sides of the beaker should be loosened and transferred to the filter paper by means of a rubber-tipped stirring rod known as a "policeman."

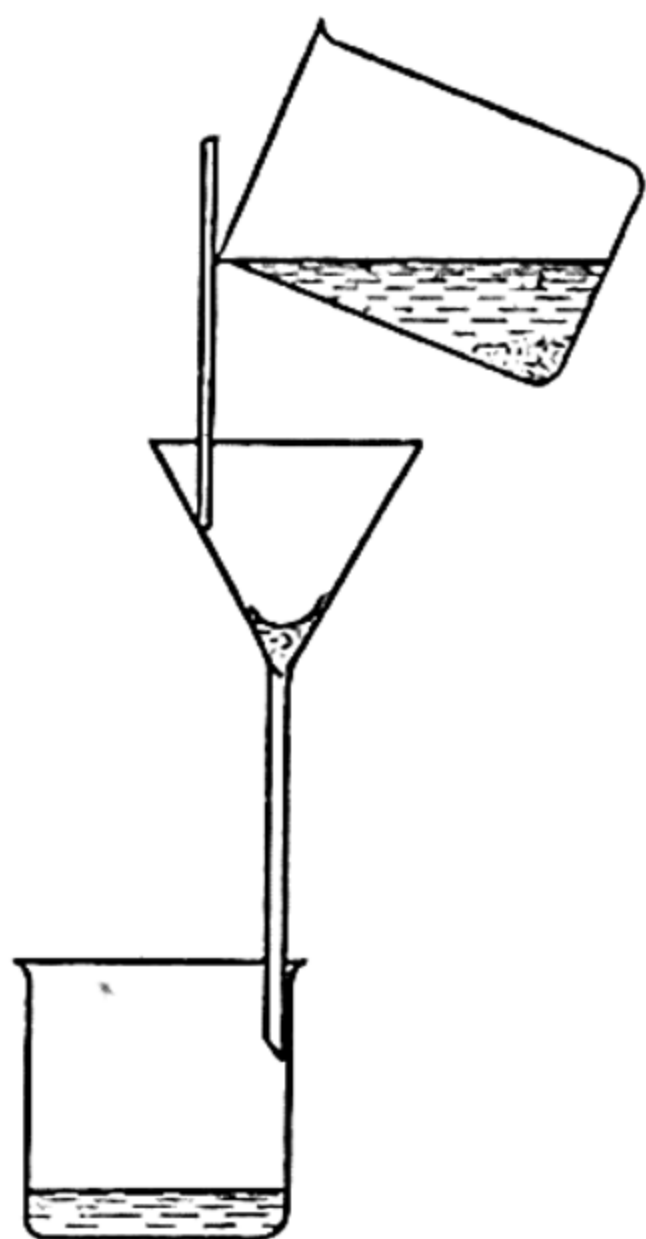


FIG. 13. Transfer of precipitate to funnel.

If washing by decantation is impracticable, the precipitate is transferred at once to the filter paper and there washed with successive, small (10-ml.) portions of the wash water until tests of the filtrate no longer show the presence of impurities. Silver nitrate is a good test reagent since in so many determinations chlorides are present and their complete removal is a good criterion of the removal of other impurities.

Specially prepared filter paper, treated with hydrochloric and hydrofluoric acids to remove ash-forming constituents, must be used. This "ashless" filter paper leaves a negligible amount of ash on ignition and no correction for filter-paper ash need be made to the final weight of the ignited product.

**Drying and Igniting.** Precipitates such as  $\text{AgCl}$ , which are decomposed at the temperature required for burning off the filter paper, are separated from the solution by filtration through a Gooch filter. This consists of a crucible with a perforated bottom, on top of which is



formed a thin layer of asbestos which serves as filtering medium. The preparation of Gooch crucibles is described under the procedure for the determination of chlorides (see page 191). Porous porcelain or fritted glass crucibles may be used in place of Gooch crucibles. In analyses of this kind the crucible, properly prepared, is dried to constant weight in a drying oven at about  $105^{\circ}\text{C}$ . and, after receiving its charge of washed precipitate, is again dried to constant weight at the same temperature.

Ashless filter papers are used whenever the precipitate is to be ignited. Meker burners or blast-lamp muffle furnaces are used for the ignition. If reducible compounds are thus ignited, the carbon resulting from the incomplete burning of the filter paper may reduce the compound; in this case it must be reoxidized and brought to constant composition. Specific directions are given under each procedure where special care in igniting precipitates must be exercised.

**Cooling and Weighing.** The dried or ignited product, contained in a previously weighed crucible, should be allowed to cool somewhat in the air, after which it is placed in a desiccator to be brought to constant temperature and moisture content. A desiccator is a device that holds in its bottom compartment a drying agent, such as  $\text{CaCl}_2$  or other desiccant, and that is provided with a shelf or tray upon which the crucibles rest. After remaining in the desiccator for a short interval the crucible may be weighed. Successive heatings and weighings are necessary until two successive weighings do not differ by more than 0.0002 gram. It can then be safely assumed that the product has reached practically constant weight.

When the weight of the dried or ignited product and its chemical composition are known, the amount of constituent which is contained in or is equivalent to it can readily be found by simple calculation.

## THE CALCULATIONS OF GRAVIMETRIC ANALYSIS

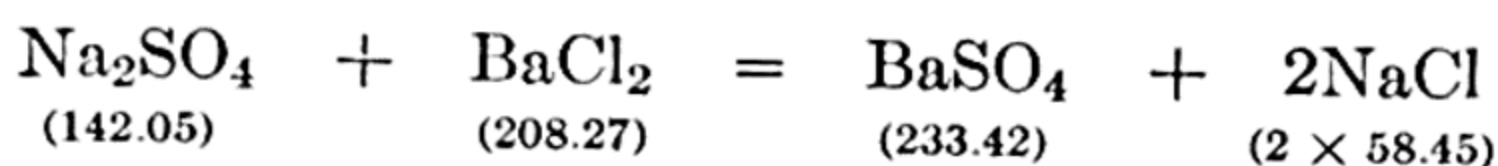
In the general discussion of the calculations of quantitative analysis presented on page 13 it was pointed out that the analytical chemist has occasion to deal with calculations of different kinds, each type based upon some general law of chemistry.

### APPLICATION OF THE LAW OF CONSTANT COMPOSITION

In the present section attention is directed specifically to the fundamental calculations based on the Law of Constant Composition and applied to gravimetric procedures. This important law, the most characteristic feature of all chemical action, states that the weights of reacting substances are proportional to their atomic or molecular weights or

simple multiples of these weights. The law is used not only to calculate the weight of reacting components but also to find the weight of constituents in a given weight of pure compound. In particular, in gravimetric analysis, the law is applied in finding the weight of constituent sought which is contained in the weight of the pure compound obtained by analysis.

A chemical equation is more than the chemist's mere statement, in symbols, that certain substances are undergoing changes to produce a new set of substances. Thus the equation

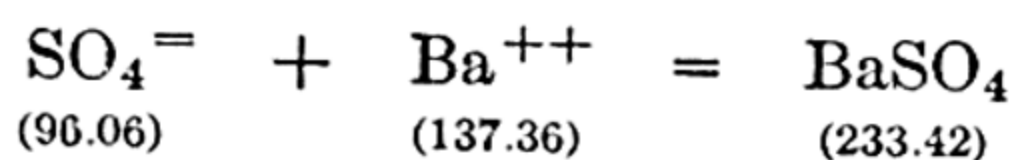


represents more than the qualitative fact that sodium sulfate reacts with barium chloride to form barium sulfate and sodium chloride. The important fact it portrays is that 142.05 parts by weight of sodium sulfate react with 208.27 parts by weight of barium chloride to give 233.42 parts of barium sulfate and  $2 \times 58.45$  parts of sodium chloride.

It is immaterial what unit of weight we choose—grams, grains, pounds, tons, etc.; in scientific work, where the metric system is in use, the gram is the unit of weight.

Since the quantities in the above equation are identical with the molecular weights and since grams are the actual weights used, the equation states that a gram-mole of sodium sulfate reacts with a gram-mole of barium chloride to form a gram-mole of barium sulfate and two gram-moles of sodium chloride.

The above molecular equation may be reduced to the following ionic form:



giving the essential components of this precipitation reaction.

Inasmuch as the chemical symbols represent the proportions by which elements or compounds react, based on oxygen = 16.000, the actual weights, in grams or other units, will be proportional to these relative combining weights.

Since, in the above equation,  $\text{Na}_2\text{SO}_4$  is to  $\text{BaSO}_4$  as 142.05 is to 233.42, any given weight of  $\text{Na}_2\text{SO}_4$  will produce a corresponding weight of  $\text{BaSO}_4$ . Thus 142.05 grams or pounds of  $\text{Na}_2\text{SO}_4$  will produce 233.42 grams or pounds of  $\text{BaSO}_4$ ; one-half of this will form 116.71 grams or, in general, any fractional part will react proportionally. From a chemical equation therefore we can calculate the weight of substance formed if we know the weight of reactant and the molecular or atomic weights. Similarly if we determine the weight of product formed we can calculate



the weight of reacting constituent. From the balanced chemical equation a proportion is set up between the molecular weights of the components concerned and the actual weights.

The fundamental arithmetical equation is a direct proportion, written thus:

$$\frac{\text{Molecular weight of reactant}}{\text{Actual weight of reactant}} : \frac{\text{Molecular weight of resultant}}{\text{Actual weight of resultant}} =$$

It is preferable to express this relationship in the form of ratios, since this mode of expression leads directly to the chemical factor discussed below.

In gravimetric analysis, as noted above, the object is to find the weight of constituent which is contained in a known weight of purified precipitate. Calculations of this kind are then best formulated in the form of ratios in this manner:

$$\frac{\text{Molecular or atomic weight of constituent sought}}{\text{Molecular weight of precipitate}} = \frac{\text{Actual weight of constituent}}{\text{Actual weight of precipitate}}$$

A simple example will illustrate this.

What is the weight of sulfate ( $\text{SO}_4$ ) contained in 0.8250 gram of  $\text{BaSO}_4$ ?

By the first mode of expression we have

$$\begin{array}{ccc} \text{SO}_4 & : & \text{BaSO}_4 = x \text{ gram} : 0.8250 \text{ gram} \\ (96.06) & & (233.42) \end{array}$$

The product of the means is equal to the product of the extremes; therefore

$$233.42x = 96.06 \times 0.8250$$

and

$$x = \frac{96.06 \times 0.8250}{233.42} = 0.3393 \text{ gram of SO}_4$$

In the form of ratios, the above problem is formulated thus:

$$\frac{\begin{array}{c} (\text{SO}_4) \\ 96.06 \\ (\text{BaSO}_4) \\ 233.42 \end{array}}{233.42} = \frac{x \text{ gram}}{0.8250 \text{ gram}}$$

from which we get

$$0.4116 = \frac{x}{0.8250}$$

and

$$x = 0.4116 \times 0.8250 = 0.3393 \text{ gram of SO}_4$$

**Moisture Determinations.** Samples of material contain more or less moisture, particularly if the samples are obtained from raw materials which are hygroscopic or have been exposed to moist atmospheres. Samples as a rule should be dried and the analytical determinations must be made on moisture-free samples, thus making it possible to report the result on a dry basis. Frequently the actual percentage of moisture must be determined and reported. The procedure for a moisture determination has already been given.

Analyses must be corrected to a moisture-free basis if the determinations are made on undried samples; on the other hand, percentages must sometimes be recalculated from a moisture-free basis to an "as received" basis. It is important to understand the method of calculation in both cases. An example will illustrate this.

Suppose a coal sample was found to contain 10 per cent of moisture and 40 per cent of volatile combustible matter; what is the percentage of this latter constituent on a dry basis? Since the dry material amounted to 90 per cent of the "as received" sample, the percentage of the volatile combustible matter is  $(0.40 \div 0.90) \times 100$  or 44.4 per cent. In the same case, if the volatile combustible matter was determined on the dry sample, and amounted to 40 per cent, its percentage on an "as received" basis is  $(0.90 \times 0.40) \times 100$  or 36.0 per cent.

Moisture determinations are important not only for the purpose of finding the amount of moisture present but more particularly in correcting percentages to a uniform common basis and in bringing the results of several analysts into agreement. Ores, limestones, cements, coal and many other materials of this character are usually analyzed for their moisture content.

**Determination of Water of Crystallization.** The determination of water of crystallization in hydrated compounds may be carried out in much the same way as the free moisture method above described, the only difference being that a higher temperature is required to remove the water of hydration. A more exact method consists in absorbing the water in a suitable apparatus; and from the increase of the absorption tube, the percentage can readily be calculated.

**Removal of Solvent.** In certain analyses, when other methods are not available the solution can be taken down to dryness by careful evaporation of the solvent and the residue weighed; from the weight the amount of constituent contained therein is determined. The salt left on removal of the solvent must of course be stable and non-volatile at the temperature used. Sulfates as a rule are more stable than the corresponding chlorides and nitrates, and for this reason the solution is

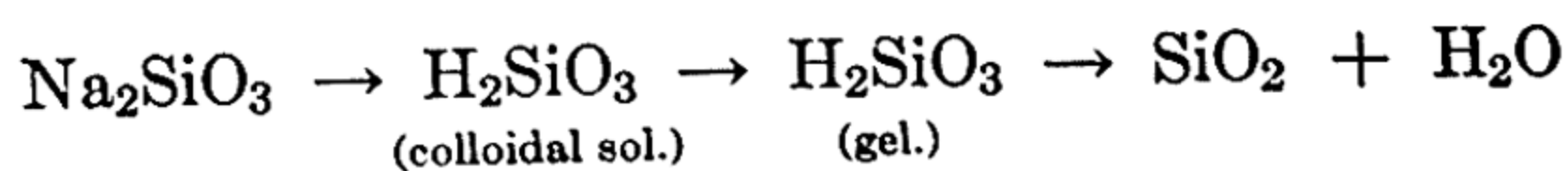


usually acidified with concentrated sulfuric acid and fumed down until a residue of the metal sulfate remains. Other elements must of course be removed before this method can be employed. The removal of interfering metals is carried out, in general, much as in the procedures of qualitative analysis.

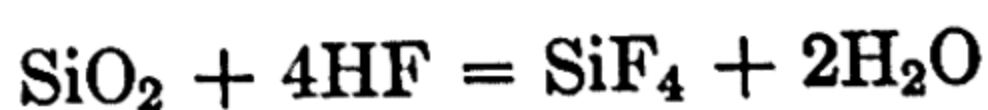
Examples of such methods are determinations of cadmium, zinc, potassium and sodium, the metal sulfate being thus obtained in a pure state and weighed. This, in fact, until quite recently, was the only available method for sodium, since no insoluble salts of sodium were known by which this element could have been quantitatively precipitated, nor are any volumetric methods possible. In the sulfate method for the determination of sodium, after the removal of other metals which precede it in the systematic scheme, the solution is acidified with sulfuric acid and evaporated to dryness. Quite frequently, potassium, which may accompany sodium, is likewise converted to the sulfate; the mixture is weighed, then redissolved and the potassium is precipitated as  $K_2PtCl_6$  or as  $KClO_4$ , and the sodium is determined by difference.

**Determination of Silica.** The exact determination of silica in natural and artificial silicate materials such as minerals and rocks, glasses, refractories, cements, slags and alloys is based ultimately on the formation and evolution of silicon tetrafluoride. When the silica is separated by dehydration from other constituents it is usually contaminated with impurities.

In the analysis of silicate-containing materials of the type of feldspar, the sample is fused with sodium carbonate and the resulting  $Na_2SiO_3$  is treated with hydrochloric acid and taken down to dryness in a platinum crucible. During this treatment the silicic acid undergoes progressive changes, passing through the colloidal state and finally becoming dehydrated to  $SiO_2$ . The changes can be indicated schematically thus:



The separation of silica by this method and the weighing of the  $SiO_2$  at this stage are not satisfactory because the silica is invariably contaminated with impurities, especially  $Fe_2O_3$  and  $Al_2O_3$ , owing to the colloidal, gelatinous nature of the silicic acid. For the exact determination of silica, the residue of impure  $SiO_2$  is treated with hydrofluoric and sulfuric acids. By this treatment the  $SiO_2$  is decomposed into  $SiF_4$ , which is volatilized from the crucible. The reaction is



The residue consists of the impurities, and by weighing the crucible before and after the HF treatment, the loss in weight represents the amount of  $\text{SiO}_2$ .

**Determination of Carbon Dioxide.** The determination of carbon dioxide is an important one in evaluating limestones, baking powders and other carbonate-containing materials, in determining the total carbon in steel and in the analysis of organic compounds. In a limestone analysis the  $\text{CO}_2$  evolved from a weighed portion of the sample is absorbed, and from the increase in weight of the absorption tube its weight and percentage can be found.

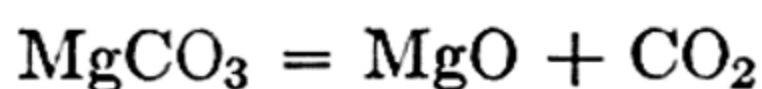
### DESCRIPTIVE OUTLINE OF LIMESTONE ANALYSIS

The rocks of the earth's crust are mainly of two types, namely, carbonate and silicate rocks. Both types furnish vast quantities of raw materials for use in various technical processes. The most important of the carbonate rocks are the limestones. A fairly pure limestone is essentially  $\text{CaCO}_3$ ; most limestones contain, besides other minerals, varying amounts of  $\text{MgCO}_3$ , these being designated as dolomitic limestones. When the amount of  $\text{MgCO}_3$  represents the composition  $\text{CaMg}(\text{CO}_3)_2$  the rock is called a dolomite. Among the impurities are silica and silicates or other minerals of iron, aluminum, titanium, manganese, etc., as well as small amounts of the alkalies.

Generally, a proximate analysis of a limestone sample furnishes the best information as to the utilization of the material. The proximate analysis consists of the following determinations: (1) loss on ignition, (2) silica, (3) combined oxides (reported as  $\text{R}_2\text{O}_3$  and consisting principally of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ), (4) calcium, (5) magnesium. A separate determination of moisture may be desired as well as a determination of  $\text{CO}_2$ .

The results are generally calculated and reported in terms of the oxides; it should be borne in mind that these reported oxides actually do not exist as such in the original sample.

**Loss on Ignition.** When a limestone is heated to about  $1100^\circ\text{C}$ ., the principal reactions which occur are the decomposition of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  with evolution of  $\text{CO}_2$ :



The evolution of  $\text{CO}_2$ , together with evolved moisture and combined water, accounts for nearly all of the loss in weight. The  $\text{CaO}$  and



MgO further react with silica and alumina to render the sample more soluble in preparation of the silica determination.

The procedure consists, in brief, of heating a weighed portion of the sample, gradually increasing the ignition temperature until about  $1100^{\circ}\text{C}$ . is reached. The ignited residue is cooled, weighed and re-ignited to constant weight. The result is calculated as percentage loss on ignition.

**Silica.** The residue from the loss on ignition determination is transferred to a casserole. The cake is broken up and the solution is evaporated to dryness. The resulting residue is treated with concentrated HCl, then with water, and digested. The precipitated silica is filtered off and washed with hot, dilute HCl and water. The filtrate and washings are again evaporated and treated as before with the exception that the silica is washed with cold dilute HCl and water. The two filter papers are combined, charred and ignited to constant weight in clean, ignited porcelain crucibles and the silica is weighed. The result is the uncorrected silica. If a more exact determination is required, the impure silica is treated with hydrofluoric acid, following the procedure previously outlined.

**Combined Oxides.** When the filtrate from the determination of silica is treated with an excess of ammonium hydroxide, a complex group precipitate is obtained. The precipitate may contain the hydrated oxides,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ ,  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  and such compounds as phosphates, arsenates, vanadates and silicates. These latter compounds exist mainly in combination with ferric iron. The silicates contain the bulk of the  $\text{SiO}_2$  not precipitated by previous acid dehydration.

In refined analyses this group precipitate is analyzed for its constituents. In a simplified procedure, the group as a whole is determined and recorded as combined oxides without reference to the amounts of individual oxides present. This determination is variously referred to as  $\text{R}_2\text{O}_3$ , ammonia precipitate, or combined oxides. The ignited product consists mainly of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and phosphates.

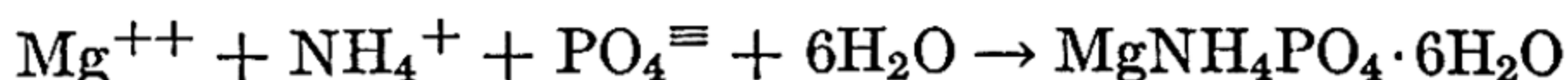
The determination is carried out by treating the filtrate from the silica determination with HCl and bromine water and then boiling. Several drops of methyl red indicator are added and the solution is treated with ammonium hydroxide until the indicator turns yellow. The precipitate is digested for several minutes, filtered, dissolved and reprecipitated in the same manner. Finally the solution is filtered, the precipitate is washed with a dilute  $\text{NH}_4\text{Cl}$  solution and ignited to constant weight. The filtrates are reserved for the subsequent determinations of calcium and magnesium.





condition for the precipitation of magnesium as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , providing the magnesium is present in moderate amounts. If magnesium is present in small amounts, ammonium salts must be destroyed before the precipitation is carried out.

The precipitate is formed by adding an excess of  $(\text{NH}_4)_2\text{HPO}_4$  first and then an excess of  $\text{NH}_4\text{OH}$ . The following reaction occurs:



The filtrate from the calcium determination is treated with  $\text{HCl}$  and an excess of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4\text{OH}$ . The precipitate so formed is allowed to stand for at least four hours and is then filtered, washed, dissolved and reprecipitated, as before, under carefully controlled conditions. The precipitate is again allowed to stand and is then filtered and washed. It is finally ignited to constant weight at  $1100^\circ\text{C}$ . and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

### DESCRIPTIVE OUTLINE OF THE ANALYSIS OF BRASS

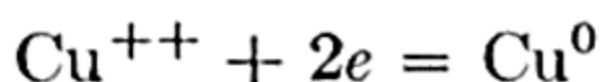
As typical of a complete, systematic analysis of an alloy, the analysis of brass is here described. Incorporated herein is also a brief discussion of the theory of electroanalysis, by which method copper is usually determined in non-ferrous alloys such as brass and bronze.

Brass is an alloy consisting principally of copper and zinc and generally containing small amounts of tin, lead and iron and possibly also aluminum and antimony. The usual analysis involves the quantitative separation and gravimetric determination of tin, lead, copper (sometimes iron) and zinc. In the usual systematic separation and determination of these metals, tin is first removed, as metastannic acid ( $\text{H}_2\text{SnO}_3$ ) and weighed as  $\text{SnO}_2$ ; any antimony present is usually determined along with the tin. Lead is next removed as lead sulfate and weighed as such. Copper is usually determined by electrodeposition. Iron, if present, is precipitated (along with aluminum, if present), as hydrated ferric oxide and ignited to ferric oxide. Finally zinc is precipitated as zinc ammonium phosphate, then ignited to and weighed as zinc pyrophosphate.

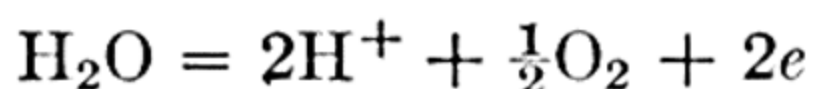
### THE THEORY OF ELECTROANALYSIS

**Electrolysis.** Under certain specified conditions, when a direct current of electricity is passed through a solution of a metallic salt, the cations are reduced to the metallic form and are deposited on the cathode and the anions are oxidized at the anode. Thus, for example, if a solution of copper sulfate is electrolyzed with a suitable current strength,

using platinum electrodes, the reaction at the cathode is a reduction of the cupric ions to metallic copper:



each ion gaining two electrons. At the anode, the  $\text{SO}_4^{=}$  ion is decomposed, liberating free oxygen, which escapes as a gas, and reproducing an equivalent amount of sulfuric acid, the net effect being the decomposition of water at this electrode:



Under suitable conditions of deposition the metal may be weighed, thus constituting a very exact and rapid method for the gravimetric determination of certain metals. The deposition of the metal and the nature of the deposit depend upon such factors as the voltage, the current density and the nature of the solution.

Whether or not metallic ions are reduced and deposited on the cathode and free elements are liberated at the anode depends upon the voltage at the electrodes. There is a minimum potential required for deposition below which no deposition takes place. This minimum potential is known as the decomposition potential of the dissolved salt in question. The decomposition potential is the algebraic sum of the deposition potential required to deposit the metal at the cathode and the potential required to produce an equivalent effect at the anode. It varies with each metal and each anion. For a given anion such as in sulfate solutions, the lower the deposition potential for a metal, the more easily will it be reduced and deposited. The metals can thus be arranged in a series, in the order of increasing ease of their deposition. The order with certain omissions is as follows: alkali metals, alkaline-earth metals, zinc, cadmium, nickel, hydrogen, copper, silver, gold. For the anions the order is nitrate, sulfate, chloride, bromide, iodide, hydroxyl. From this it can be seen that copper, for instance, is deposited at a lower potential than hydrogen or zinc, and that the potential required to deposit copper from a sulfate solution is less than from a nitrate solution. Numerical values, in volts, have been determined for the deposition-potentials for the series of metals and non-metallic elements for solutions containing equivalent (normal) concentrations of the ions. In practice, however, such data can be applied only approximately because, as electrolysis proceeds, the concentration of ions gradually diminishes and the voltage must be increased. A knowledge of the potential series (the electromotive series of metals) is nevertheless most useful in finding the order and relative ease with which the metals can be separated and deposited.



In addition to this minimum potential required for deposition the additional voltage necessary to overcome the resistance of the solution must be taken into consideration in electrolysis.

**Overvoltage.** The discharge of ions at the electrodes is further complicated by what is known as overvoltage. From the position of hydrogen in the above series, it appears that hydrogen is more easily liberated than the metals above it (zinc, for example), and it should not ordinarily be possible to plate out zinc in preference to liberation of hydrogen. Hydrogen, however, is more easily liberated when its ions are in contact with certain metals than with others. The difference in voltage required to liberate hydrogen on a metal electrode during electrolysis and that required to liberate it on a platinized platinum electrode is called the hydrogen overvoltage for that metal. If the overvoltage is large and near that of the deposition voltage of the metal, the metal may deposit before hydrogen, or hydrogen itself may be evolved ahead of its turn when metals below it are being electrolyzed. On account of the high overvoltage of hydrogen on zinc it is quite possible, with a large current and too low an acidity, to plate out zinc during the electrolysis of copper solutions.

**Faraday's Laws.** The amount of metallic and non-metallic element liberated at the electrodes depends upon the quantity of electricity passed and can be calculated from the laws of Faraday. Faraday's first law states that the weight of any element liberated at an electrode is proportional to the quantity of electricity passing through the solution. His second law states that equivalent weights of different elements are liberated by the same quantity of electricity. A gram-equivalent weight of a substance is that weight in grams which will react directly or indirectly with 1.008 grams of hydrogen. For metals, it is the gram-atomic weight divided by the valence change when the metallic ion is reduced.

The unit of current strength is the ampere and is that amount of current which will deposit 0.001118 gram of silver per second from a solution of silver nitrate. The quantity of electricity is measured in coulombs. (A coulomb is one ampere flowing for one second.) Coulombs are related to amperes by the equation

$$\text{Coulombs} = \text{Amperes} \times \text{time in seconds}$$

A current strength of 10 amperes, for example, flowing for 5 seconds will result in the passage of 50 coulombs.

According to Faraday's second law, in order to deposit a gram-equivalent or 107.88 grams of silver, there will be required  $107.88/0.001118$  or 96,500 coulombs. In general it has been found that 96,500 coulombs

are required to liberate a gram-equivalent weight of any element or compound. The quantity, 96,500 coulombs, is called a faraday. A faraday will therefore liberate 107.88 grams of silver or 31.78 grams of copper, or 1.008 grams of hydrogen or 8.000 grams of oxygen from solutions of these ions.

It should be noted that equivalent quantities of elements are liberated at each electrode. Thus in the electrolysis of a solution of copper sulfate, 96,500 coulombs (one faraday) will simultaneously deposit 31.78 grams of copper on the cathode and liberate 8.000 grams of oxygen at the anode.

In electrochemical analysis, where the discharge of metallic ions must be complete, a direct calculation of the total current required cannot be made, because as electrolysis proceeds the concentration of ions diminishes and a somewhat larger current is required for the deposition of the metal than that calculated from Faraday's law on the assumption that the ionic concentration remains constant.

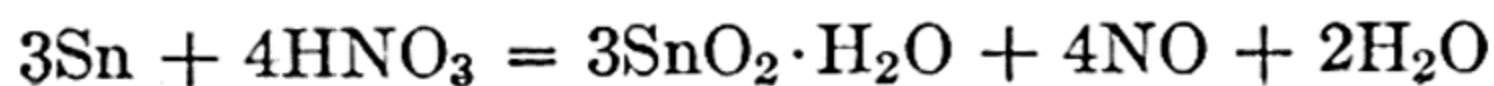
**Current Density.** Since the deposit is to be weighed, it must firmly adhere to the electrode. The chief factor influencing the character of the deposit is the current density. Current density is the amperage divided by the area of the electrode. The unit chosen for the electrode area is one square decimeter (100 square centimeters). Current densities are expressed as amperes per square decimeter. For the decomposition of copper the current density must be low in order to give a good deposit, about 2 amperes per square decimeter of cathode area. For cylindrical gauze cathodes the area is computed as the total area, both inside and outside, of a plane cylinder of like dimensions.

In order to prevent impoverishment of ions in the immediate vicinity of the electrode the solution should be stirred, either by use of a separate stirrer or by rotating the anode by means of an electric motor.

Most metals are deposited at the cathode in the metallic condition. Lead and manganese, however, are usually deposited as  $\text{PbO}_2$  and  $\text{MnO}_2$  on the anode. Electrolysis is usually made from nitrate or sulfate solutions, because free chlorine liberated from chloride solutions attacks the platinum electrodes.

## OUTLINE OF PROCEDURE

**Determination of Tin.** When a brass is treated with nitric acid, copper, zinc and lead pass into solution as the nitrates, but tin is converted to a colloidal hydrated stannic oxide (or metastannic acid,  $\text{H}_2\text{SnO}_3$ ) which is insoluble in nitric acid:





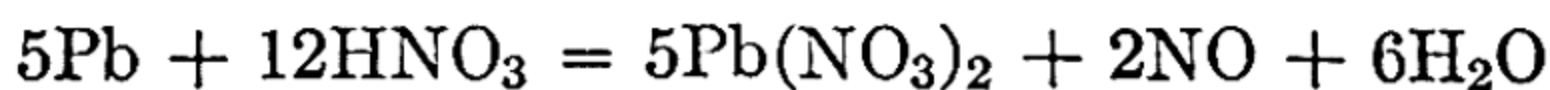
As is common with colloidal precipitates, the hydrated stannic oxide easily adsorbs and coprecipitates other ions in the solution. This adsorption may be partially eliminated by digesting in concentrated nitric acid, in which case the precipitate is somewhat coagulated, thus cutting down the large adsorbing area. In the evaporation, the precipitate is not taken to dryness. If such happens, it is very difficult to wash impurities from the precipitate.

The digested precipitate is filtered off, using paper pulp to prevent particles from running through the filter, and the oxide is dehydrated and ignited to  $\text{SnO}_2$ .

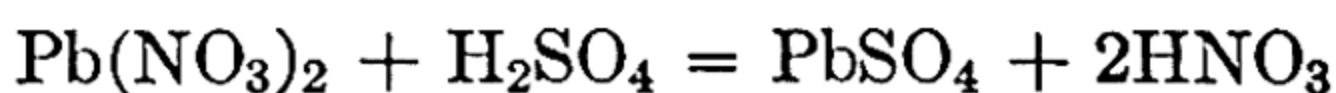
The percentage of tin in the sample is found by multiplying the weight of  $\text{SnO}_2$  by the factor for Sn in  $\text{SnO}_2$ , 0.7877, dividing by the weight of sample and multiplying by 100.

**Determination of Lead.** Two good methods are commonly used for the determination of lead. In the one method the lead is precipitated as the sulfate by evaporating the solution containing lead and  $\text{H}_2\text{SO}_4$  to fumes of  $\text{SO}_3$ . The other method involves the electrolytic precipitation as lead dioxide,  $\text{PbO}_2$ , on the anode in a strong nitric acid solution. Other methods such as precipitation as  $\text{PbMoO}_4$  or  $\text{PbCrO}_4$  are not so desirable because they introduce other elements into the filtrate and these may lead to complications in subsequent separations.

The initial attack of the alloy by nitric acid converts the lead to lead nitrate:



Upon addition of sulfuric acid and evaporation to fumes, the lead is precipitated as the sulfate and nitric acid is eliminated:



The filtrate and washings from the tin determination is treated with 5 ml. of concentrated  $\text{H}_2\text{SO}_4$  and carefully evaporated over a low flame until dense white fumes of  $\text{SO}_3$  appear. The precipitated  $\text{PbSO}_4$  is separated from the copper and zinc by use of a previously prepared Gooch crucible. The crucible is ignited at a relatively low temperature ( $500^\circ$ – $600^\circ\text{C}.$ ). The  $\text{PbSO}_4$  is weighed as such; from such data the percentage of lead in the alloy can readily be calculated.

**Determination of Copper.** The most convenient and one of the best methods for determining copper in alloys and of separating it from zinc is by electrolytic precipitation. In this method, the cupric ion in solution is electrolyzed, using platinum electrodes. The copper that is plated out is quantitatively determined by weighing the cathode before and after the reaction.





## CALCULATIONS OF INDIRECT ANALYSIS

Frequently, in chemical analysis, two closely related elements are present in the same sample. They will therefore usually react in the same way toward reagents. Thus if, in the determination of iron, aluminum had been present in the iron sample, the precipitate would have consisted of a mixture of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ , and on ignition a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  would have been obtained. In the chloride determination, bromides and iodides, if present, would have precipitated as  $\text{AgBr}$  and  $\text{AgI}$  along with  $\text{AgCl}$ . The alkali metals, sodium and potassium, are often associated with each other, giving on analysis a residue which consists of a mixture of the sulfates or the chlorides of these two elements. Similarly, mixtures of oxalates, carbonates, sulfates and sulfides are sometimes encountered in gravimetric analysis.

Obviously, if a determination is to be made for the amount of each constituent present, a further experiment must be performed in order to find the amount of each present. There are various ways by which this may be done.

In the first example cited, that of the mixture of iron and aluminum, experimentally the difficulty can be overcome by first precipitating the mixture with  $\text{NH}_4\text{OH}$ , igniting the mixed  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  to  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  and weighing the mixture of oxides. The mixture of oxides may then be dissolved or another sample taken and, by a separate (volumetric) analysis, the amount of iron can be determined. Then, calculating the weight of  $\text{Fe}_2\text{O}_3$  equivalent to the amount of iron found and subtracting this from the total weight of mixed oxides gives by difference the weight of  $\text{Al}_2\text{O}_3$ .

In the case of materials containing potassium and sodium, these two elements will be left in solution after the removal of metals which precede them in the qualitative grouping. The solution may then be fumed down with sulfuric acid, and the residue, consisting of a mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , weighed. The residue is then redissolved and the potassium precipitated as  $\text{K}_2\text{PtCl}_6$  or as  $\text{KClO}_4$ . From these data the weight of potassium can be found, which, when recalculated as  $\text{K}_2\text{SO}_4$  and subtracted from the weight of residue, gives, as the difference, the weight of  $\text{Na}_2\text{SO}_4$ .

Instead of determining one of the constituents by a separate procedure and calculating the other by difference, as illustrated in the foregoing examples, it is possible with certain mixtures which have a common constituent to make a separate determination of this common constituent. The calculations are then more complicated. A sample calculation is made in the following problem.

A sample of material contained, among other constituents, a chloride and a bromide. A weighed portion was dissolved and treated with an excess of  $\text{AgNO}_3$ , precipitating a mixture of  $\text{AgCl}$  and  $\text{AgBr}$  weighing 0.8413 gram. By a separate analysis of this mixture the total amount of silver was found to be 0.5678 gram. What are the weights of chlorine and bromine in the sample?

We know the total weight of the mixture of  $\text{AgCl}$  and  $\text{AgBr}$  and the total weight of silver which is partly combined with the chlorine and partly with the bromine. In order to find the amounts of chlorine and bromine, we must first calculate the separate weights of  $\text{AgCl}$  and of  $\text{AgBr}$ . Letting  $x$  stand for the weight of  $\text{AgCl}$  and  $y$  for the weight of  $\text{AgBr}$ , we have the equation

$$x + y = 0.8413 \text{ gram} \quad (1)$$

The weight of silver combined as  $\text{AgCl}$  is found from the relation

$$\text{Ag} : \text{AgCl} = \text{Weight of Ag in AgCl} : x$$

or

$$\frac{\text{Ag}}{\text{AgCl}} x = \text{Weight of Ag in AgCl}$$

and the weight of silver combined as  $\text{AgBr}$  is

$$\text{Ag} : \text{AgBr} = \text{Weight of Ag in AgBr} : y$$

or

$$\frac{\text{Ag}}{\text{AgBr}} y = \text{Weight of Ag in AgBr}$$

The total weight of silver, which has been found by experiment to be 0.5678 gram, is therefore related to the weights of  $\text{AgCl}$  and  $\text{AgBr}$  by the equation

$$\frac{\text{Ag}}{\text{AgCl}} x + \frac{\text{Ag}}{\text{AgBr}} y = 0.5678 \text{ gram} \quad (2)$$

Inserting the proper atomic and molecular weights, equation (2) becomes

$$\frac{107.88}{143.34} x + \frac{107.88}{187.80} y = 0.5678$$

Using the above ratios as chemical factors of Ag in  $\text{AgCl}$  and of Ag in  $\text{AgBr}$ , we have the two equations

$$0.7526x + 0.5744y = 0.5678$$

$$x + y = 0.8413$$



Solving these simultaneous equations, by the elimination of  $y$  we have

$$\begin{array}{rcl} 0.7526x + 0.5744y & = & 0.5678 \\ 0.5744x + 0.5744y & = & 0.4832 \\ \hline 0.1782x & & = 0.0846 \\ x & & = 0.4747 \end{array}$$

Therefore  $x$ , the weight of AgCl, is equal to 0.4747 gram. The value for  $y$  may now be found from equation (1):

$$\begin{aligned} x + y &= 0.8413 \\ y &= 0.8413 - 0.4747 \\ y &= 0.3666 \end{aligned}$$

Therefore  $y$ , the weight of AgBr, is equal to 0.3666 gram. Finally the amount of chlorine is  $(\text{Cl}/\text{AgCl}) \times 0.4747 = 0.1174$  gram, and the amount of bromine is  $(\text{Br}/\text{AgBr}) \times 0.3666 = 0.1560$  gram.

In general, data which involve a common constituent such as a mixture of silver salts, mixed sulfates of the alkalies or alkaline earths, mixed carbonates, etc., must be resolved into two equations, one of which usually embodies the chemical factors, and these equations must then be solved simultaneously.

## PROBLEM SET 14

### INDIRECT ANALYSIS

1. A mixture of AgBr and AgCl weighing 1.2500 gram was treated with chlorine in order to convert AgBr into AgCl. After such treatment the mass weighed 1.1800 gram. What are the percentages of Cl and Br in the sample?

*Ans.* 10.07 per cent Br; 18.88 per cent Cl

2. A mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  weighing 0.3050 gram was obtained by igniting the mixture of hydroxides obtained from a 1.0000-gram sample of limestone. A separate analysis of the limestone for iron gave 6.58 per cent. What is the percentage of aluminum?

3. A mixture of NaCl and  $\text{NH}_4\text{Cl}$  weighing 0.4500 gram was dissolved in water, treated with chloroplatinic acid, the  $(\text{NH}_4)_2\text{PtCl}_6$  filtered off and ignited, yielding 0.1063 gram of platinum. What are the percentages of NaCl and  $\text{NH}_4\text{Cl}$  represented in the mixture?

*Ans.* 12.86 per cent NaCl; 87.13 per cent  $\text{NH}_4\text{Cl}$

4. A certain mixture of AgCl and AgBr weighs 0.9000 gram. The silver in this mixture, determined independently, weighs 0.6500 gram. What are the weights of AgCl and AgBr in the mixture?

5. A sample consisting of a mixture of  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  weighing 1.0537 grams, when dissolved and treated with  $\text{BaCl}_2$ , gave a precipitate of  $\text{BaSO}_4$  weighing 1.5874 grams. What are the percentages of potassium and sodium?

*Ans.* 17.80 per cent Na; 20.20 per cent K

6. A 1.0000-gram sample of feldspar rock yielded a mixture of KCl and NaCl weighing 0.2875 gram. After dissolving the mixed chlorides in water and adding AgNO<sub>3</sub>, the AgCl obtained weighed 0.6927 gram. Find the percentages of K and Na in the sample.

7. An analysis of a limestone showed it to contain 98 per cent of a mixture of CaCO<sub>3</sub> and MgCO<sub>3</sub>. The CO<sub>2</sub> in the sample was 50.55 per cent. Calculate the percentages of MgCO<sub>3</sub> and CaCO<sub>3</sub>.

*Ans.* 90.86 per cent MgCO<sub>3</sub>; 7.14 per cent CaCO<sub>3</sub>

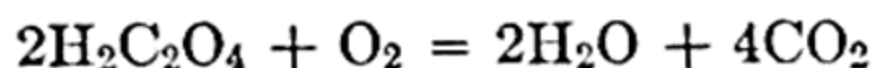
8. A 1.0000-gram sample of a certain material gives a mixture of SrC<sub>2</sub>O<sub>4</sub> and CaC<sub>2</sub>O<sub>4</sub> which weighs 0.5000 gram. By a volumetric method the oxalate content of the precipitate is found to be 0.2815 gram. What are the percentages of CaO and SrO in the mixture?

9. What is the percentage of K<sub>2</sub>O, Na<sub>2</sub>O and SO<sub>3</sub> in a sample made up by mixing equal gram-molecular parts of pure K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>?

*Ans.* 29.78 per cent K<sub>2</sub>O; 19.60 per cent Na<sub>2</sub>O; 50.62 per cent SO<sub>3</sub>

10. In an organic combustion analysis, oxygen was passed over an organic compound containing C, H and O. The carbon was oxidized to CO<sub>2</sub> and absorbed in a KOH absorption tube; the hydrogen was oxidized to H<sub>2</sub>O and was absorbed in a CaCl<sub>2</sub> absorption tube. The sample weighed 0.7510 gram. The gain in weight of the CaCl<sub>2</sub> tube was 0.0987 gram and that of the KOH tube 0.7024 gram. Calculate the percentages of C, H and O in the sample.

11. If a 0.7500-gram sample of pure H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is placed in an organic combustion furnace and burned in a stream of oxygen, according to the reaction



what weight of H<sub>2</sub>O and CO<sub>2</sub> should be collected in the absorption tubes?

*Ans.* 0.1501 gram H<sub>2</sub>O; 0.7332 gram CO<sub>2</sub>

12. In what proportions should CaCO<sub>3</sub> and MgCO<sub>3</sub> be mixed in order to make a sample containing 50.00 per cent CO<sub>2</sub>?

13. A silicate rock sample weighing 1.0000 gram yielded 0.2500 gram of a mixture of Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. After dissolving these sulfates and precipitating the potassium as K<sub>2</sub>PtCl<sub>6</sub>, a weight of 0.4210 gram of K<sub>2</sub>PtCl<sub>6</sub> was obtained. Calculate the percentages of K and Na in the sample.

*Ans.* 6.77 per cent K; 3.21 per cent Na

14. A mixture of MgCO<sub>3</sub> and SrCO<sub>3</sub> weighed 1.7500 grams. If these carbonates are converted to sulfates and the sulfate mixture weighs 2.2500 grams, what are the percentages of MgCO<sub>3</sub> and SrCO<sub>3</sub> in the sample?

15. A 0.2500-gram mixture of Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> was obtained from a 1.1250-gram sample of silicate rock. After dissolving these sulfates and precipitating with Ba<sup>++</sup> as BaSO<sub>4</sub>, a weight of 0.3870 gram of BaSO<sub>4</sub> was obtained. What are the percentages of K<sub>2</sub>O and Na<sub>2</sub>O in the sample?

*Ans.* 7.47 per cent Na<sub>2</sub>O; 2.76 per cent K<sub>2</sub>O

16. A mine owner ships a cargo of iron ore which analyzes 2.7 per cent moisture and 69.5 per cent Fe<sub>2</sub>O<sub>3</sub> on a wet basis at the mine. The chemist at the blast furnace finds that the moisture content has increased to 7.3 per cent during transit. What percentages of Fe<sub>2</sub>O<sub>3</sub> should be reported on (a) the wet and (b) the dry basis?

17. A sample of coal was dried, losing 8 per cent of its weight through evaporation of water. One gram of this dried sample gave 0.0173 gram of BaSO<sub>4</sub> when the sulfur was converted to sulfate and precipitated as BaSO<sub>4</sub>. What was the percentage of sulfur in the original coal?

*Ans.* 0.22 per cent



18. A sample of coal, as received, contained 8.2 per cent moisture; when the dried sample was analyzed for other constituents it was found to contain (a) 23.9 per cent volatile combustible matter, (b) 59.0 per cent fixed carbon and (c) 17.2 per cent ash. What are the percentages of these constituents in the sample as received?

19. A sample of iron ore was found to contain 6.5 per cent moisture and 57.83 per cent iron. What is the percentage of iron in the sample when calculated to the dry basis? Ans. 61.84 per cent

20. A certain soluble sulfate sample contained 2.13 per cent moisture. On analysis 0.5682 gram of the original sample gave 0.7059 gram of  $\text{BaSO}_4$ . What was the percentage of  $\text{SO}_3$  in the moisture-free sample?

### SUMMARY OF ANALYTICAL METHODS

In final summary, it will be evident to the student that for any given element or ion, generally two or more methods of determination are possible and, as a general rule, a choice is offered between a gravimetric and a volumetric method. Table IX, based on a similar one in Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, summarizes the

TABLE IX  
METHODS MOST COMMONLY USED IN DETERMINING THE ELEMENTS

Element	Gravimetric	Volumetric
Aluminum	$\text{Al}_2\text{O}_3$ , $\text{AlPO}_4$ , Al-quinolate	Iodometric, neutralization
Antimony	$\text{Sb}_2\text{S}_3$ , $\text{Sb}_2\text{O}_4$	Oxidation, iodometric, iodimetric
Arsenic	$\text{As}_2\text{S}_3$ , $\text{As}_2\text{S}_5$	Ag on $\text{Ag}_3\text{AsO}_4$ , iodometric, iodimetric
Barium	$\text{BaSO}_4$ , $\text{BaCrO}_4$	Iodometric
Beryllium	$\text{BeO}$	
Bismuth	$\text{Bi}_2\text{O}_3$ , $\text{BiOCl}$	Colorimetric
Boron	Fixed $\text{B}_2\text{O}_3$	Neutralization
Bromine	$\text{AgBr}$	Iodometric, precipitation
Cadmium	$\text{Cd}$ , $\text{CdSO}_4$	
Calcium	$\text{CaO}$ , $\text{CaSO}_4$	Oxidation of the oxalate
Carbon	Fixed $\text{CO}_2$	
Cesium	$\text{CsCl}$ , $\text{CsClO}_4$ , $\text{Cs}_2\text{PtCl}_6$	
Chlorine	$\text{AgCl}$	Iodometric, precipitation
Chromium	$\text{Cr}_2\text{O}_3$	Reduction, iodometric, colorimetric
Cobalt	$\text{CoSO}_4$ , $\text{Co}$	
Columbium	$\text{Cb}_2\text{O}_6$	Oxidation
Copper	$\text{Cu}$ , $\text{CuCNS}$	Iodometric, oxidation, colorimetric
Fluorine	$\text{PbClF}$ , $\text{CaF}_2$	Neutralization, colorimetric
Gallium	$\text{Ga}_2\text{O}_3$	
Germanium	$\text{GeO}_2$ , $\text{Mg}_2\text{GeO}_4$	
Gold	$\text{Au}$	
Hafnium	$\text{HfO}_2$	
Hydrogen	$\text{H}_2\text{O}$	
Indium	$\text{In}_2\text{O}_3$	
Iodine	$\text{AgI}$	Iodometric, precipitation

TABLE IX—Continued

## METHODS MOST COMMONLY USED IN DETERMINING THE ELEMENTS

Element	Gravimetric	Volumetric
Iridium	Ir	
Iron	Fe <sub>2</sub> O <sub>3</sub>	Oxidation, reduction, iodometric
Lead	PbSO <sub>4</sub> , PbO <sub>2</sub>	Iodometric, precipitation
Lithium	Li <sub>2</sub> SO <sub>4</sub>	
Magnesium	MgO, Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> , MgSO <sub>4</sub> , Mg-quinolate	Iodometric, neutralization
Manganese	MnSO <sub>4</sub> , MnS, Mn <sub>3</sub> O <sub>4</sub>	Oxidation, reduction, colorimetric
Mercury	HgS, Hg <sub>2</sub> Cl <sub>2</sub> , Hg	Precipitation
Molybdenum	MoO <sub>3</sub> , PbMoO <sub>4</sub>	Oxidation, colorimetric
Nickel	Ni-dimethylglyoxime, Ni	Cyanide titration
Nitrogen		Colorimetric, neutralization (NA <sub>3</sub> )
Osmium	Os	
Oxygen	H <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub>	
Palladium	Pd-dimethylglyoxime, Pd	
Phosphorus	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Neutralization, colorimetric
Platinum	Pt	
Potassium	KCl, K <sub>2</sub> PtCl <sub>6</sub> , KClO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub>	
Radium	Electroscopic	
Rare gases	Gasometric	
Rare earths *	Oxides	
Rhenium	AgReO <sub>4</sub> , Re	Neutralization
Rhodium	Rh	
Rubidium	RbCl, Rb <sub>2</sub> PtCl <sub>6</sub> , RbClO <sub>4</sub>	
Ruthenium	Ru	
Scandium	Sc <sub>2</sub> O <sub>3</sub>	
Selenium	Se	Oxidation, iodometric
Silicon	SiO <sub>2</sub>	
Silver	AgCl, Ag	Precipitation
Sodium	NaCl, Na <sub>2</sub> SO <sub>4</sub>	
Strontium	SrO, SrSO <sub>4</sub>	
Sulfur	BaSO <sub>4</sub>	Precipitation, iodometric, iodimetric
Tantalum	Ta <sub>2</sub> O <sub>5</sub>	
Tellurium	Te	Oxidation, iodometric
Thallium	Tl <sub>2</sub> CrO <sub>4</sub> , Tl <sub>2</sub> O <sub>3</sub> , Tl <sub>2</sub> PtCl <sub>6</sub>	Oxidation, iodometric
Thorium	ThO <sub>2</sub>	
Tin	SnO <sub>2</sub>	Iodometric
Titanium	TiO <sub>2</sub>	Oxidation, colorimetric
Tungsten	WO <sub>3</sub>	Neutralization
Uranium	U <sub>3</sub> O <sub>8</sub>	Oxidation
Vanadium	V <sub>2</sub> O <sub>5</sub>	Oxidation, reduction
Yttrium	Y <sub>2</sub> O <sub>3</sub>	
Zinc	ZnO, Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> , ZnS	Precipitation
Zirconium	ZrO <sub>2</sub> , ZrPO <sub>4</sub>	

\* Elements 57-71. All are trivalent in their principal valences.



methods most commonly used. Under the heading of gravimetric methods, the element can be weighed as metal, as oxide, or as a salt of definite composition. The volumetric methods involve neutralization, oxidation or reduction and precipitation or are some type of colorimetric determination.

### CALCULATION OF FORMULAS AND ATOMIC WEIGHTS

**Formulas.** An important application of quantitative analysis is the use of analytical data to determine the empirical formulas of pure compounds and minerals. The analysis of a pure chemical compound will show the weight of each element in the weight of sample taken. The percentage composition can then be easily calculated. If the actual weight of each element is divided by the atomic weight of that element, the quotient will be the number of gram-atoms of each element present. These gram-atomic weights bear a simple relation to one another in that there will be a common divisor; and, if each gram-atomic weight is divided by this common divisor, the ratio of the numbers of atoms of the elements present can be found. The percentages obtained from analysis may be used in the same way as the actual weights, since the percentage of an element is directly proportional to the weight of that element present.

As a simple example, suppose that a 1.0000-gram sample of a pure salt is analyzed and found to be composed of 0.3934 gram of sodium and 0.6066 gram of chlorine. Dividing 0.3934 by the atomic weight of sodium, 22.997, gives 0.01711 gram-atom of sodium, and 0.6066 divided by 35.457 gives 0.01711 gram-atom of chlorine. There are just as many gram-atoms of sodium as there are of chlorine and, consequently, just as many atoms of one element as of the other. The ratio of the number of sodium atoms to the number of chlorine atoms in the compound, then, is 1 : 1; and the simplest formula is NaCl.

The formula thus obtained is merely the empirical formula, that is, the simplest ratio of the number of atoms of each element which make up the compound. The actual molecular formula may be a simple multiple of the empirical formula. A molecular-weight determination must be made in order to assign the proper formula to the compound. Such determinations need not be too accurate, since it is only necessary to distinguish between the empirical formula weight and its simple multiples. Various physical-chemical methods are available for determining molecular weights.

In the Dumas method a known volume of a gaseous substance is weighed under controlled and readily measured conditions of tempera-

ture and pressure. Then, recalling that one gram-molecular weight, or mole, of a gas occupies 22.41 liters at 0°C. and 760 millimeters pressure, the weight of gas occupying this gram-molecular volume under these standard conditions can be calculated. This weight is the gram-molecular weight of the gas. For example, a Dumas bulb of 300.0 ml. capacity is filled at 25°C. and 740 millimeters pressure with a gas of unknown molecular weight. The weight of the gas in the bulb is found to be 0.526 gram. To calculate the molecular weight the volume of gas must first be corrected to standard conditions. The student will recall that the volume of a gas varies directly as the absolute temperature and inversely as the pressure. The expression for the correction of volume is then

$$300.0 \text{ ml.} \times \frac{273^{\circ}\text{C.}}{273^{\circ}\text{C.} + 25^{\circ}\text{C.}} \times \frac{740 \text{ mm.}}{760 \text{ mm.}}$$

which, when solved, gives 267.6 ml. as the volume corrected to 0°C. and 760 millimeters pressure. This volume of gas weighed 0.526 gram. To find the weight of 22.41 liters, or the gram-molecular weight of the gas, multiply 0.526 gram by 22,410 ml. and divide the product by 267.6 ml., the corrected volume. This gives 44.0 grams as the weight of the gas which occupies 22.41 liters, so 44.0 is the molecular weight of the gas.

It is also possible, as in the Victor Meyer method, to vaporize a weighed amount of volatile liquid and measure under known conditions of temperature and pressure the volume of vapor produced. This volume is converted to standard conditions, 0°C. and 760 millimeters pressure. The weight of substance necessary to produce 22.41 liters of gas under these conditions may then be calculated. Attention should be called, however, to the fact that in laboratory determinations by the Victor Meyer method, the vapor from the volatile liquid displaces a volume of air which in turn is collected in a gas buret over water. In converting this volume of displaced air to standard conditions, the vapor pressure of the water in the buret must be subtracted from the observed barometric pressure. With this exception, the method of calculation is the same as that for the Dumas molecular weight determination.

A liquid to which has been added a soluble, non-volatile non-electrolyte has a higher boiling point than the pure liquid. This principle is the basis of still another method for the determination of molecular weights. A 1 molal solution of such a substance in water has a boiling point of 100.52°C., the boiling point rise being directly proportional to the amount of solute present. Now, if a weighed amount of substance of unknown molecular weight is added to a known weight of boiling



solvent, and the increase in boiling point is measured, we have sufficient data to calculate the unknown molecular weight. To illustrate, 1.2 grams of solute was added to 17.5 grams of boiling water; the boiling point rise was  $0.51^{\circ}\text{C}$ . Since a 1 molal solution contains one mole of solute per 1000 grams of solvent, a conversion to a basis of 1000 grams of water is made first:  $1.2 : 17.5 = x : 1000$ . The value of 68.6 grams is obtained for  $x$ . This amount of solute, however, produces only  $0.51^{\circ}\text{C}$ . boiling point rise, whereas the molal boiling point rise for water is  $0.52^{\circ}\text{C}$ . If 68.6 grams is multiplied by  $0.52^{\circ}\text{C}$ . and the product is divided by  $0.51^{\circ}\text{C}$ ., 69.9 grams is found to be that weight of solute which must be added to 1000 grams of water to raise its boiling point  $0.52^{\circ}\text{C}$ .; this weight is the molecular weight of the unknown solute.

The measured lowering of the freezing point caused by the addition of a soluble non-electrolyte to a pure solvent can be similarly used to calculate molecular weights. The molal freezing point lowering for water is  $1.86^{\circ}\text{C}$ . This method is probably the most accurate for the determination of molecular weights in solutions, and has helped establish the true formulas of many organic substances from data of the analyses.

Once we have found the empirical formula of a compound from percentage composition data, and the molecular weight by some physical-chemical means, it is a simple process to decide on the proper molecular formula. To illustrate, a calculation of the results of a combustion analysis of a pure organic compound showed its empirical formula to be  $\text{CH}_2\text{O}$ . When a freezing-point molecular-weight determination was made, the molecular weight of the compound was found to be 180. The sum of the atomic weights of the empirical formula is 30, whereas the true molecular weight is 180. By inspection, we can see therefore that the true molecular formula is six times as great, or  $\text{C}_6\text{H}_{12}\text{O}_6$ .

**Atomic Weights.** The entire structure of chemistry as an exact science rests upon the precision with which the atomic weights of the elements are known. The analytical procedures by which the atomic weights are arrived at are unquestionably the most precise of all quantitative determinations. One method consists in making an exact quantitative determination of the constituent in a very carefully purified sample of a compound containing the element the atomic weight of which is to be determined. Such a quantitative determination may not, however, give the true atomic weight but rather a multiple or submultiple of it. What is really obtained is the combining weight and not necessarily the atomic weight.

The combining weight is the proportion in which one element will combine with another; the atomic weight is the weight of an atom rela-



tive to that of oxygen taken as 16.0000. To illustrate, if we analyze water we find that for every 1.0080 grams of hydrogen there are 8.0000 grams of oxygen; the combining weight of oxygen is therefore 8.0000. If we determine the amount of copper and oxygen in black copper oxide, we find that the copper and oxygen are united in the ratio of 31.78 : 8; whereas in the red oxide of copper the combining proportions of copper to oxygen as determined by experiment are 63.57 : 8. With the atomic weight of oxygen fixed at 16.0000, the combining weights of copper are 63.57 and 127.14. To arrive at the atomic weight of copper, we must decide which of these combining weights is the atomic weight.

To decide whether the combining weight of an element is its atomic weight, or what multiple or submultiple of the combining weight to use, involves consideration of other criteria and the application of certain rules and laws. Among these are: (1) the Law of Dulong and Petit, which states that the specific heat of a solid element multiplied by its atomic weight is, in most cases, a constant having the value 6.4; (2) Avogadro's Hypothesis, that equal volumes of gases (under the same conditions of pressure and temperature) contain the same number of molecules; (3) the Periodic Law, in which the element is placed in its proper family relationship; (4) most of the elements, in the gaseous state, are diatomic; (5) the least common multiple of several combining weights for the same element will, in many cases, indicate the atomic weight.

Applying the last rule to the case of copper previously referred to, where the combining weights are 63.57 and 127.14 respectively, this would indicate the atomic weight of copper to be 63.57. This can be checked by the rule of specific heats; for if we multiply the specific heat of copper, 0.092, by 63.57 we get approximately 6, in sufficient agreement with the constant 6.4 to show that the selected combining weight is the true atomic weight.

During the first half of the nineteenth century, after Dalton's atomic theory had been advanced and the combining weights of elements had been worked out with fair accuracy, especially by Berzelius, chemists were not in agreement as to the true atomic weights. The hypothesis of Avogadro had not been accepted because it seemed limited in its applicability, and Dulong and Petit's Law had proved to be quite inconclusive in practice. It was the contributions of the organic synthetists, Williamson, Hofmann, Wurtz and Kekulé, in fixing the formulas of simple substances like water, ammonia and methane, that paved the way for final agreement as to which multiple of the combining weight was the atomic weight. At a meeting in 1860 of the prominent chemists of that time, Cannizzaro summed up the existing knowledge, clarified



the interpretations of Avogadro's Hypothesis, and made some suggestions as to how to develop a system of atomic weights.

He proposed that the molecular weights of the volatile compounds of the elements should be determined. On analyzing these compounds, it could then be found what part of the molecular weight should be attributed to each element. In selecting the atomic weight, the smallest weight of an element found in the molecular weights of its compounds should be chosen.

Now that criteria had been established for determining which multiple or submultiple of the combining weight was the atomic weight, chemists entered again upon the problem of more accurate determinations. It had been more than twenty years since the work of Berzelius, and great improvements in apparatus and procedure had been made. Stas, a Belgian chemist, refined analytical techniques to a degree never before attained. His materials were carefully purified, his balances were of much greater accuracy, and his manipulations were conducted with utmost precautions. During the early part of this century, Richards, in the laboratories of Harvard University, further refined the methods of atomic weight determinations.

The more general method of atomic weight determinations used today is the chemical conversion of one pure compound to another. This is possible because now we can be certain of the chemical equivalency of the two compounds. The ratio of the equivalent weights of the two compounds is calculated. Then, by using those atomic weights previously determined, the atomic weight of another element may be found.

Let us take as an example Richards' determination of the atomic weight of lithium. He weighed out many samples of carefully purified lithium chloride on balances which were accurate to the hundred-thousandths of a gram. These samples were dissolved and caused to react with silver nitrate. From seven reported experiments he calculated that 1.000000 gram of silver is equivalent to 0.392992 gram of lithium chloride. Then the following relationship was used:

$$\text{Weight LiCl} : \text{Weight Ag} = \text{Molecular Weight LiCl} : \text{Molecular Weight Ag}$$

The atomic weight of silver was accurately known to be 107.880, and that of chlorine had been determined as 35.457. The atomic weight of lithium is now the only unknown and can readily be calculated by substituting  $(x + 35.457)$  for the molecular weight of lithium chloride. On the basis of this work Richards found the atomic weight of lithium to be 6.939.

Most atomic weight determinations now consist in an elaboration of the care and precautions in carrying out the analytical procedures.

In 1941 G. P. Baxter of Harvard University was the Chairman of the Committee on Atomic Weights of the International Union of Chemistry. He and the other members, M. Guichard of the Sorbonne, Paris, O. Hönigschmid of Munich, Germany, and R. Whytlaw-Gray of the University of Leeds, Leeds, England, each year consider the recent work on atomic weight determinations, and revise the table of atomic weights to conform to the most probable values.

## PROBLEM SET 15

## FORMULAS AND ATOMIC WEIGHTS

1. A sample of pure  $\text{KMnO}_4$  was found to contain 39.65 per cent of potassium. Taking  $\text{K} = 39.10$  and  $\text{O} = 16.00$ , calculate the atomic weight of manganese.

*Ans.* 54.89

2. A 0.7500-gram sample of a certain metal yielded 1.8430 grams of bromide. If the metal is monovalent, what is its atomic weight? If the metal is divalent, what is its atomic weight?

3. A 0.5000-gram sample of a certain pure compound yielded 0.1900 gram of chlorine; a 0.2500-gram portion of the salt upon the addition of  $(\text{NH}_4)_2\text{SO}_4$  and the ignition of the precipitate gave 0.2800 gram of  $\text{BaSO}_4$ . What was the compound?

*Ans.*  $\text{BaCl}_2$

4. If, by an organic combustion, the percentage composition of a certain organic compound becomes established as 77.92 per cent carbon, 11.68 per cent hydrogen, and 10.40 per cent oxygen (by difference), what are the ratios, carbon: hydrogen: oxygen? What is the empirical formula?

5. The boiling point of a solution of 0.987 gram of a non-volatile non-electrolyte in 15.60 grams of water was  $100.32^\circ\text{C}$ . Calculate the molecular weight of the solute.

*Ans.* 102.8

6. A compound of unknown molecular weight was dissolved in water and the freezing point of the solution was determined. The following data were obtained.

Weight of sample	1.308 grams
Weight of water	14.65 grams
Freezing point of the solution	$1.44^\circ\text{C}$ .

Calculate the molality of the solution and the molecular weight of the solute.

7. If 3.2912 grams of pure silver yield 5.7295 grams of  $\text{AgBr}$ , what is the atomic weight of bromine?

*Ans.* 79.92

8. In converting 8.5875 grams of  $\text{AgBr}$  to  $\text{AgI}$ , there was found to be an increase of 2.1494 grams. Calculate the atomic weight of iodine, assuming the atomic weights of  $\text{Ag}$  and  $\text{Br}$  to be 107.880 and 79.916 respectively.

9. A sample of a pure compound gave on analysis 42.90 per cent zinc, 20.35 per cent phosphorus, and 36.75 per cent oxygen. What is the empirical formula of the compound?

*Ans.*  $\text{Zn}_2\text{P}_2\text{O}_7$

10. If 0.5000 gram of a certain mineral contains 0.2392 gram of copper, 0.0974 gram of arsenic, and 0.1635 gram of sulfur, what is the formula of the mineral?

11. A compound when analyzed was found to have the following composition: carbon, 10.06 per cent; hydrogen, 0.84 per cent; chlorine, 89.10 per cent. A Victor



Meyer molecular weight determination was run. The vaporization of 0.1638 gram of the liquid displaced 35.62 ml. of air, which was collected over water and measured at 23.0°C. and 732.6 millimeters pressure. The vapor pressure of water at 23.0°C. is 21.1 millimeters. What is the formula of the compound? *Ans.*  $\text{CHCl}_3$

12. A chemist conducting an organic combustion analysis with an organic compound finds that with a 1.0000-gram sample, 2.5200 grams of  $\text{CO}_2$  and 0.0885 gram of water are obtained. Calculate the percentages of C, H, and O in the sample, and from this the atomic ratio of these elements. Give the empirical formula of the compound.

13. Given the formula of a pure compound as  $\text{Mg}_2\text{P}_2\text{O}_7$ , calculate the percentage composition. *Ans.* 21.84 per cent Mg; 27.86 per cent P; 50.30 per cent O

14. An evacuated Dumas bulb, when filled with a gas at 32.0°C. and 735 millimeters pressure, gained 0.483 grams in weight. If the volume of the bulb had been previously found to be 283.5 ml., what is the molecular weight of the gas?

15. In making an atomic weight determination of sodium, five 1.0000-gram samples of pure NaCl yielded as an average of five closely agreeing results, 2.4521 grams of AgCl. Taking  $\text{Cl} = 35.457$  and  $\text{Ag} = 107.880$ , what is the atomic weight of sodium? *Ans.* 22.997

16. Richards and Hoover found that the ratio of the weights of equivalent amounts of  $\text{Na}_2\text{SO}_4$  to  $\text{Na}_2\text{CO}_3$  was 1.340155 to 1.00000. Previously Richards had determined the atomic weights of sodium and carbon as 22.995 and 12.005 respectively. On the basis of his data, calculate the atomic weight of sulfur.

17. In 1941 the atomic weight of holmium, one of the rare earths, was changed by the International Committee. Hönigschmid and Hirshbold-Wittner compared silver with holmium chloride and found that the ratio  $\text{HoCl}_3/3\text{Ag}$  was equal to 0.83829. Assuming the atomic weight of silver to be 107.880 and that of chlorine to be 35.457, what is the revised atomic weight of holmium? *Ans.* 164.94

18. The atomic weights of silver and bromine are 107.880 and 79.916 respectively. From the ratios  $\text{FeBr}_2/2\text{Ag} = 0.999645$  and  $\text{FeBr}_2/2\text{AgBr} = 0.574244$ , calculate the atomic weight of iron.

19. One of the most important ratios used in calculating atomic weights is the  $\text{AgCl}/\text{Ag}$  ratio. The following are the data which Richards and Anderegg obtained in their experimental determinations of the ratio.

Ag	AgCl
6.22211 grams	8.26738 grams
5.16568	6.86361
5.18476	6.88876
5.92279	7.86933
5.00706	6.65256

Calculate each  $\text{AgCl}/\text{Ag}$  ratio, and the average ratio; and, assuming the atomic weight of silver to be 107.880, calculate the atomic weight of chlorine.

*Ans.* 1.32871; 1.32869; 1.32866; 1.32864; 1.32864; 1.32867 avg.; 35.457 at. wt. Cl.

20. If the atomic weight of sodium is 22.997 and  $\text{Na}_2\text{SO}_4$  contains 44.055 per cent oxygen, what is the atomic weight of sulfur?

## APPENDIX

### THE LITERATURE OF ANALYTICAL CHEMISTRY

Modern chemistry owes its rapid advance, in part, to the exact measurements developed by the analytical chemist. The pioneers in the field such as Lavoisier, Berzelius, Stas, Rose and Fresenius were followed, in later years, by a host of others who brought to the present high state the art and technique of analytical chemistry. The record of their accomplishments may be found in the chemical literature and if the student of chemistry is to keep abreast of current developments in this field he must be on the alert for the published information. Especially if he wants to look up a method of analysis, a new piece of analytical apparatus or some theoretical topic, he must know how to use the analytical literature.

When an investigator perfects a new method of analysis, designs a new apparatus or contributes in some other way to the advancement of analytical chemistry, he publishes his findings, as an original paper, in one of the chemical journals, preferably one on analytical chemistry, such as *Zeitschrift für analytical Chemie* (the oldest, first published in 1841 by Fresenius), *The Analyst* (a British journal begun in 1877), *Annales de chimie analytique et de chimie appliquée et Revue de chimie analytique réunies*, the leading French journal in analytical chemistry, or, if he is an American, the Analytical Edition of *Industrial and Engineering Chemistry*. Soon after publication, the article is abstracted and a brief abstract is published in an abstracting journal, of which *Chemical Abstracts* is the most important. *British Abstracts* and *Chemische Zentralblatt* are the other two abstracting journals. Later on, the article may be reviewed in a review journal and ultimately, if the original idea has merit, it finds its way into reference books, textbooks, and manuals of analysis.

When the chemist, therefore, is searching for analytical information, he searches both the journal literature and the reference books and similar publications. It is best to start with the current biweekly issues of *Chemical Abstracts* (section 7 and specialized fields), then refer to the annual indexes, finally working back to the decennial indexes. The other abstracting journals should also be checked. Such a search will reveal information which may not have been incorporated into books on analytical chemistry.

The books on analytical chemistry are very numerous and, if assembled, would fill many shelves in a library. They cover many phases of chemical analysis, both theoretical and applied, in many languages. Below is given a selected list of analytical books, most of which should be available in college libraries; they will supply the answer of many a student's question: "What is a good book on such and such a topic in quantitative analysis?"

I. M. KOLTHOFF and E. B. SANDELL, *Textbook of Quantitative Analysis*, New York, The Macmillan Co., 1936.

W. F. HILLEBRAND and G. E. F. LUNDELL, *Applied Inorganic Analysis*, New York, John Wiley & Sons, Inc., 1929.



- F. P. LEADWELL and W. T. HALL, *Analytical Chemistry*, Vol. II, New York, John Wiley & Sons, Inc., 1942.
- W. C. PIERCE and E. L. HAENISCH, *Quantitative Analysis*, New York, John Wiley & Sons, Inc., 2nd ed., 1940.
- H. H. WILLARD and N. H. FURMAN, *Elementary Quantitative Analysis*, New York, D. Van Nostrand Co., 1940.
- N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, New York, D. Van Nostrand Co., 1939.
- G. E. F. LUNDELL, J. I. HOFFMAN and H. A. BRIGHT, *Chemical Analysis of Iron and Steel*, New York, John Wiley & Sons, Inc., 1931.
- G. LUNGE and C. A. KEANE, *Technical Methods of Chemical Analysis*, New York, D. Van Nostrand Co., 1924-1931.
- R. C. GRIFFEN, *Technical Methods of Analysis*, New York, McGraw-Hill Book Co., 1921.
- A. H. WHITE, *Technical Gas and Fuel Analysis*, New York, McGraw-Hill Book Co., 1920.
- I. M. KOLTHOFF and N. H. FURMAN, *Potentiometric Titrations*, New York, John Wiley & Sons, Inc., 2nd ed., 1931.
- I. M. KOLTHOFF and H. A. LAITENEN, *pH and Electro Titrations*, New York, John Wiley & Sons, Inc., 2nd ed., 1941.
- L. M. DENNIS and M. L. NICHOLS, *Gas Analysis*, New York, The Macmillan Co., 1929.
- C. J. ENGELDER, *Gas, Fuel and Oil Analysis*, New York, John Wiley & Sons, Inc., 1931.
- G. F. SMITH, *Special and Instrumental Methods of Analysis*, Ann Arbor, Mich., Edwards Brothers, 1937.
- F. D. SNELL and C. T. SNELL, *Colorimetric Methods of Analysis*, New York, D. Van Nostrand Co., 1936.
- G. V. HEVESY, *Chemical Analysis by X-Rays and Its Applications*, New York, McGraw-Hill Book Co., 1932.
- C. A. BROWNE and F. W. ZERBAN, *Physical and Chemical Methods of Sugar Analysis*, New York, John Wiley & Sons, Inc., 3rd ed., 1941.
- I. M. KOLTHOFF, *Acid-Base Indicators*, trans. by C. Rosenblum, New York, The Macmillan Co., 4th ed., 1937.
- M. B. JACOBS, *Chemical Analysis of Foods and Food Products*, New York, D. Van Nostrand Co., 1938.
- AMERICAN SOCIETY FOR TESTING MATERIALS, *Methods for the Chemical Analysis of Metals*, frequently revised, Philadelphia.
- C. M. JOHNSON, *Rapid Methods for the Chemical Analysis of Special Steels*, New York, John Wiley & Sons, Inc., 4th ed., 1930.
- U. S. STEEL CORPORATION, CARNEGIE STEEL CO., *Methods of the Chemists of the U. S. Steel Corporation: Methods for Sampling and Analysis of Alloy Steels*, Pittsburgh, Pa., 1921.

## THE PLAN OF THE COURSE—SUGGESTIONS TO THE INSTRUCTOR

In a one-semester course in quantitative analysis where, quite possibly, the time allotted might be reduced to one lecture, one recitation and six to eight hours of laboratory practice a week, the problem of finding sufficient time to cover the desired assignments is a perplexing one. Furthermore, students whose curriculum includes only a brief course presumably will terminate their analytical training with the completion of such a course. It is therefore important that a judicious selection of subject matter be made. The author ventures here to make a few suggestions which might prove helpful in planning the content and distribution of assignments to fit the needs of various classes.

**The Lectures.** These obviously will deal with the theoretical aspects, elaborate on the technique, give further explanatory details concerning the procedures and possibly offer opportunity for lecture demonstrations.

**The Recitations.** If but one recitation period a week is available, drill on problems and calculations seems the best utilization of the time. To provide for this, the text supplies fifteen weekly problem sets, designed to keep pace with the laboratory work. The author's practice has been to make individual assignments for each student at the start of the semester, covering the entire semester's work, assigning for home study five odd-numbered problems (with answers) and five even-numbered problems (without answers) out of each set of twenty for each weekly assignment. The work is submitted regularly each week and the classroom hour is partly devoted to solving problems, and partly to a written quiz, using the unanswered problems for distribution among the class.

If a second recitation period is scheduled, the time might be used in quizzes on the laboratory work.

**The Laboratory Schedule.** Here there is considerable flexibility in the procedures presented in this book and the instructor can make suitable selection to meet his limitations of time. Here is the sequence the author follows:

1. Preliminary work on the balance.
2. Acid-base titrations (soda ash and potassium acid phthalate samples).
3. Dichromate determination of iron; followed by
4. Permanganate determination of iron with same sample of iron ore.
5. Volumetric determination of calcium (to be later checked by the gravimetric method).
6. Iodimetric arsenic determination.
7. Iodometric copper determination.
8. Volumetric chloride determination; followed by
9. Gravimetric chloride determination on same sample.
10. Gravimetric iron determination.
11. Gravimetric sulfate determination; and when time permits
12. Gravimetric calcium determination.
13. Gravimetric magnesium or phosphate determination.



The use of the same sample of iron ore, calcium and chloride reduces the number of separate samples to a minimum, lessens the administrative and expense burden and arouses the students' interest in comparative methods of analysis.

This suggested program is geared to the pace of the average student. Any over-time required by the slow worker or careless student will have to be provided for separately.

## REAGENTS AND SUPPLIES

### (a) LIQUID REAGENTS FOR GENERAL USE

Acetic Acid,  $\text{HC}_2\text{H}_3\text{O}_2$ .

Alcohol, Ethyl,  $\text{C}_2\text{H}_5\text{OH}$ , 95 per cent.

Ammonium Hydroxide,  $\text{NH}_4\text{OH}$ , Concentrated. The concentrated "ammonia," sp. gr. 0.90, containing 28.33 per cent  $\text{NH}_3$  by weight.

Ammonium Molybdate,  $(\text{NH}_4)_2\text{MoO}_4$ . Add 100 grams of molybdic oxide to 400 ml. of cold water and then treat, with constant stirring, with 80 ml. of concentrated  $\text{NH}_4\text{OH}$ . Allow to stand for several hours and then filter into a solution of 400 ml. of concentrated  $\text{HNO}_3$  in 600 ml. of water. After several days, filter if a residue is present. (For  $\text{PO}_4$  determination.)

Ammonium Nitrate,  $\text{NH}_4\text{NO}_3$ , 10 grams per liter of solution.

Ammonium Oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . 40 grams of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  per liter of solution. (For Ca determination.)

Barium Chloride,  $\text{BaCl}_2$ . 20 grams of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  per liter of solution. (For  $\text{SO}_4$  determination.)

Bromine Water,  $\text{Br}_2$ . Saturated solution. (For Fe determination.)

Diammonium Hydrogen Phosphate,  $(\text{NH}_4)_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . 20 grams per 100 ml. of solution. (For Mg determination.)

Hydrochloric Acid,  $\text{HCl}$ , Concentrated. C. P. reagent. Sp. gr. 1.19, containing 37.23 per cent of pure  $\text{HCl}$  by weight.

Magnesia Mixture. 50 grams of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 100 grams of  $\text{NH}_4\text{Cl}$  dissolved in 500 ml. of water, to which is added 100 ml. of concentrated  $\text{NH}_4\text{OH}$  and the volume made up to 1 liter with distilled water. Filter before using. (For  $\text{PO}_4$  determination.)

Mercuric Chloride,  $\text{HgCl}_2$ . 50 grams of  $\text{HgCl}_2$  per liter of solution.

Nitric Acid,  $\text{HNO}_3$ , Concentrated. C. P. reagent. Sp. gr. 1.42, containing 69.77 per cent of  $\text{HNO}_3$  by weight.

Silver Nitrate,  $\text{AgNO}_3$ . Precipitating agent for chloride determination. 20 grams of  $\text{AgNO}_3$  per liter of solution. (For Cl determination.)

Silver Nitrate,  $\text{AgNO}_3$ . Test reagent. 10 grams of  $\text{AgNO}_3$  and 10 ml. of concentrated  $\text{HNO}_3$  per liter of solution.

Stannous Chloride,  $\text{SnCl}_2$ . 115 grams of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 170 ml. of concentrated  $\text{HCl}$  and diluted to 1 liter. Add a few pieces of metallic tin to prevent oxidation of the reagent. (For Fe determination.)

Sulfuric Acid,  $\text{H}_2\text{SO}_4$ , Concentrated. C. P. reagent. Sp. gr. 1.84, containing 95.6 per cent of  $\text{H}_2\text{SO}_4$  by weight.

Sulfuric Acid, Concentrated. Commercial, for making cleaning mixture. The better grade (C. P.) may be used.



**(b) SOLID REAGENTS FOR GENERAL USE**

To be supplied to reagent shelves, distributed by the instructor or dispensed from the supply room.

Ammonium Chloride,  $\text{NH}_4\text{Cl}$ .  
Ammonium Nitrate,  $\text{NH}_4\text{NO}_3$ .  
Asbestos, ground, for Gooch crucibles.  
Calcium Chloride, crude, for desiccators.  
Litmus Paper, in vials, neutral, or red and blue.  
Silver Nitrate,  $\text{AgNO}_3$ .  
Sodium Bicarbonate,  $\text{NaHCO}_3$ .  
Sodium Dichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7$ , commercial, for cleaning mixture.  
Stopcock grease.  
Vaseline for desiccators.  
Zinc, pure, 20–30 mesh, for Jones reductor.

**(c) REAGENTS FOR PREPARATION OF STANDARD SOLUTIONS**

Sodium Hydroxide and Hydrochloric Acid. For standard base and acid.  
Potassium Dichromate. Can be obtained pure and use directly as a primary standard.  
Ferrous Sulfate or Ferrous Ammonium Sulfate.  
Potassium Permanganate.  
Oxalic Acid.  
(Ceric Sulfate).  
Arsenious Oxide or Sodium Arsenite.  
Iodine.  
Sodium Thiosulfate.  
Silver Nitrate.  
Potassium Thiocyanate. Can be purified and used as a primary standard.

**(d) REAGENTS FOR STANDARDIZATION**

Sodium Carbonate. For  $\text{HCl}$  standardization.  
Potassium Acid Phthalate. For  $\text{NaOH}$  standardization if an independent standardization is assigned.  
Iron Wire. For  $\text{K}_2\text{Cr}_2\text{O}_7$  if the latter is to be independently standardized.  
Sodium Oxalate. For  $\text{KMnO}_4$  standardization.  
Arsenious Oxide. For iodine standardization.  
Copper Foil. For sodium thiosulfate standardization, if desired.  
Sodium Chloride. For  $\text{AgNO}_3$  standardization.  
Silver Nitrate. For  $\text{KCNS}$  standardization, if necessary.

**(e) INDICATORS**

Methyl Orange, ordinary. Dissolve 1 gram of the dye in hot water and dilute to 1 liter. The modified indicator is to be used in acid-base titrations.

Methyl Orange, modified. In separate beakers dissolve 1 gram of methyl orange in 500 ml. of hot water and 1.4 grams of xylene cyanole FF in 500 ml. of water. Mix

measured volumes of each solution (1 ml. of each) and test with approximately 0.1 *N* acid and base for color change. Vary the proportions of the two solutions until a mixture is obtained which gives the sharpest possible color change. When the correct ratio is established, mix the two solutions in proper proportions.

**Methyl Red.** Dissolve 2 grams of the dye in 500 ml. of 95 per cent alcohol and dilute to a liter.

**Phenolphthalein.** Dissolve 10 grams of the dye in 500 ml. of 95 per cent alcohol and dilute to a liter.

**Diphenylamine Sulfonate.** For 100 ml. of the indicator solution, weigh out 0.32 gram of barium diphenylamine sulfonate, add 1 gram of  $\text{Na}_2\text{SO}_4$  and 100 ml. of water, shake, allow the  $\text{BaSO}_4$  to settle and use the supernatant liquid.

**Ortho-Phenanthroline-Ferrous Complex.** Employed only if the ceric sulfate method is used. The indicator can be purchased from the G. Frederick Smith Chemical Company, Columbus, Ohio.

**Starch Solution.** Stir 5 grams of soluble starch into 20 to 25 ml. of water and thoroughly mix until a uniform paste forms. Pour this into 500 ml. of boiling water. When cool add 10 grams of KI.

**Dichlorofluorescein.** Dissolve 0.1 gram of the reagent in 100 ml. of 70 per cent alcohol.

**Ferric Alum.** To be prepared by student as needed for the Volhard method for silver.



## DENSITY OF STRONG ACIDS AT 15°C. IN VACUO

(According to Lunge, Isler, Naef, and Marchlewsky)

Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>		HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205	.....	33.07	27.95	1.440	74.64	54.07
1.210	.....	33.80	28.58	1.445	75.94	54.55
1.215	.....	34.53	29.21	1.450	77.24	55.03
1.220	.....	35.26	29.84	1.455	78.56	55.50
1.225	.....	36.01	30.48	1.460	79.94	55.97
1.230	.....	36.76	31.11	1.465	81.38	56.43

Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight $\text{HNO}_3$	Per Cent by Weight $\text{H}_2\text{SO}_4$	Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight $\text{H}_2\text{SO}_4$	Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight $\text{H}_2\text{SO}_4$
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525	.....	62.06	1.665	74.24	1.805	87.60
1.530	.....	62.53	1.670	74.66	1.810	88.30
1.535	.....	63.00	1.675	75.08	1.815	89.16
1.540	.....	63.43	1.680	75.50	1.820	90.05
1.545	.....	63.85	1.685	75.94	1.825	91.00
1.550	.....	64.26	1.690	76.38	1.830	92.10
1.555	.....	64.67	1.695	76.76	1.835	93.56
1.560	.....	65.20	1.700	77.17	1.840	95.60
1.565	.....	65.65	1.705	77.60	1.8405	95.95
1.570	.....	66.09	1.710	78.04	1.8410	96.38
1.575	.....	66.53	1.715	78.48	1.8415	97.35
1.580	.....	66.95	1.720	78.92	1.8410	98.20
1.585	.....	67.40	1.725	79.36	1.8405	98.52
1.590	.....	67.83	1.730	79.80	1.8400	98.72
1.595	.....	68.26	1.735	80.24	1.8395	98.77
1.600	.....	68.70	1.740	80.68	1.8390	99.12
1.605	.....	69.13	1.745	81.12	1.8385	99.31

Taken from Treadwell-Hall, *Analytical Chemistry*, Vol. II, 9th ed., published by John Wiley & Sons. Reprinted with permission.



## DENSITY OF AMMONIA SOLUTIONS AT 15°C.

(According to Lunge and Wiernik)

Specific Gravity	Per Cent NH <sub>3</sub>	Specific Gravity	Per Cent NH <sub>3</sub>
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

Taken from Treadwell-Hall, *Analytical Chemistry*, Vol. II, 9th ed., published by John Wiley & Sons. Reprinted with permission.

## DENSITY OF WATER

Temper- ature, Deg. C.	Density	Temper- ature, Deg. C.	Density	Temper- ature, Deg. C.	Density
0	0.99987	22	780	43	107
1	993	23	756	44	066
2	997	24	732	45	0.99025
3	999	25	0.99707	46	0.98982
4	1.00000	26	681	47	940
5	0.99999	27	654	48	896
6	997	28	626	49	852
7	993	29	597	50	0.98807
8	988	30	0.99567	51	762
9	981	31	537	52	715
10	0.99973	32	505	53	669
11	963	33	473	54	621
12	952	34	440	55	0.98573
13	940	35	0.99406	60	324
14	927	36	371	65	059
15	0.99913	37	336	70	0.97781
16	897	38	299	75	489
17	880	39	262	80	0.97183
18	862	40	0.99224	85	0.96865
19	843	41	186	90	534
20	0.99823	42	147	95	192
21	802				



## DATA AND REPORT FORMS\*

## VOLUMETRIC DETERMINATION OF.....

Sample No.....

Date.....

## DATA

## COMPARISON OF SOLUTIONS

	1	2	3	4
.....burette reading at start	.....	.....	.....	.....
.....burette reading at finish	.....	.....	.....	.....
ml. of.....used	.....	.....	.....	.....
.....burette reading at start	.....	.....	.....	.....
.....burette reading at finish	.....	.....	.....	.....
ml. of.....used	.....	.....	.....	.....

## STANDARDIZATION

	1	2	3
Initial weight of tube and standard			
or			
Weight of tare with standard.....	.....	.....	.....
Final weight of tube and standard			
or			
Weight of tare.....	.....	.....	.....
Weight of primary standard.....	.....	.....	.....
	1	2	3
.....burette reading at start	.....	.....	.....
.....burette reading at finish	.....	.....	.....
ml. of.....used	.....	.....	.....
.....burette reading at start	.....	.....	.....
.....burette reading at finish	.....	.....	.....
ml. of.....used	.....	.....	.....

## ANALYSIS

	1	2	3
Initial weight of tube and sample			
or			
Weight of tare with sample.....	.....	.....	.....
Final weight of tube and sample			
or			
Weight of tare.....	.....	.....	.....
Weight of sample.....	.....	.....	.....
	1	2	3
.....burette reading at start	.....	.....	.....
.....burette reading at finish	.....	.....	.....
ml. of.....used	.....	.....	.....
.....burette reading at start	.....	.....	.....
.....burette reading at finish	.....	.....	.....
ml. of.....used	.....	.....	.....

\* Sample pages from the author's *Laboratory Record Book of Quantitative Analysis*.

## REPORT OF VOLUMETRIC ANALYSIS

Determination of.....

Student's Sample Number.....Instructor's Sample Number.....

## Results of Standardization

.....titre of.....solution = .....

Normality of.....solution = .....

.....titre of.....solution = .....

Normality of.....solution = .....

## Results of Analysis

Run No.

1

2

3

Per Cent Found.....

Correct Per Cent.....

Difference.....

Precision in parts per 1000... .. high low .....

Remarks by Student.....

Date.....Instructor's Name and Lab. Section.....

Grade.....Student's Signature.....

To be retained by Instructor

To be returned to Student

Determination of.....

Run No.

1

2

3

Precision in parts per 1000. .... high low .....

Remarks by Instructor.....

Date.....Instructor's Signature.....

Grade.....Student's Signature.....



GRAVIMETRIC DETERMINATION OF.....

Sample No..... Date.....

DATA

	I	2	3
Initial weight of tube and sample			
or			
Weight of tare with sample.....	.....	.....	.....
Final weight of tube and sample			
or			
Weight of tare.....	_____	_____	_____
Weight of sample.....	.....	.....	.....
	I	2	3
Weight of crucible.....	.....	.....	.....
Weight of crucible.....	.....	.....	.....
Weight of crucible.....	.....	.....	.....
	I	2	3
Weight of crucible with precipitate.....	.....	.....	.....
Weight of crucible with precipitate.....	.....	.....	.....
Weight of crucible with precipitate.....	.....	.....	.....
Weight of crucible with precipitate	_____	_____	_____
Weight of Precipitate.....	.....	.....	.....

RESULTS

Per cent of..... = .....%.....%

Average = .....%

Remarks.....  
.....

Approved by.....

## REPORT OF GRAVIMETRIC ANALYSIS

Determination of.....

Student's Sample Number.....Instructor's Sample Number.....

Run No.	1	2	3
Per Cent Found.....	.....	.....	.....
Correct Per Cent.....	_____	_____	_____
Difference.....	.....	.....	.....
Precision in parts per 1000.	..... high low	..... high low	..... high low

Remarks by Student.....

.....

.....

Date.....Instructor's Name and Lab. Section.....

Grade.....Student's Signature.....

To be retained by Instructor

To be returned to Student

Determination of.....

Run No.	1	2	3
Precision in parts per 1000..	..... high low	..... high low	..... high low

Remarks by Instructor.....

.....

.....

Date..... Instructor's Signature.....

Grade..... Student's Signature.....



PERIODIC TABLE OF THE ELEMENTS

Group	0	I	II	III	IV	V	VI	VII	VIII
Type Formulas		$R_2 - RH$	$RO - RH_2$	$R_2O_3 - RH_3$	$RO_2 - RH_4$	$R_2O_5 - RH_5$	$RO_3 - H_2R$	$R_2O_7 - HR$	
Series 1		H 1.0080							
2	He 4.003	Li 6.940	Be 9.02	B 10.82	C 12.010	N 14.008	O 16.000	F 19.00	
3	Ne 20.183	Na 22.997	Mg 24.32	Al 26.97	Si 28.06	P 30.98	S 32.06	Cl 35.457	
4	A 39.944	K 39.096	Ca 40.08	Sc 45.10	Ti 47.90	V 50.95	Cr 52.01	Mn 54.93	Fe 55.84 Co 58.94 Ni 58.69
5		Cu 63.57	Zn 65.38	Ga 69.72	Ge 72.6	As 74.91	Se 78.96	Br 79.916	
6	Kr 83.7	Rb 85.44	Sr 87.63	Yt 88.92	Zr 91.22	Cb 92.91	Mo 95.95		Ru 101.7 Rh 102.91 Pd 106.7
7		Ag 107.880	Cd 112.41	In 114.76	Sn 118.70	Sb 121.76	Te 127.61	I 126.92	
8	Xe 131.3	Cs 132.91	Ba 137.36	La 138.92	Ce 140.13	[Positions between			
9				brackets occupied by elements of the rare earth group					
10			not yet definitely assigned.]	Hf 178.6		Ta 181.4	W 183.92		Os 191.5 Ir 193.1 Pt 195.23
11		Au 197.2	Hg 200.61	Tl 204.39	Pb 207.22	Bi 209.00			
12	Rn 222.0		Ra 225.97		Th 232.12		U 238.14		

## CHEMICAL FACTORS \*

Sought	Found	Factor	Log	Sought	Found	Factor	Log
Ag	AgBr.....	0.5744	9.7593	Ba	BaCl <sub>2</sub> ·2H <sub>2</sub> O...	0.5621	9.7493
	AgCl.....	0.7526	9.8766		BaCO <sub>3</sub> .....	0.6961	9.8426
	AgCN.....	0.8055	9.9060		BaCrO <sub>4</sub> .....	0.5422	9.7341
	AgI.....	0.4595	9.6622		BaSO <sub>4</sub> .....	0.5885	9.7697
	AgNO <sub>3</sub> .....	0.6350	9.8028		BaSiF <sub>6</sub> .....	0.4912	9.6913
	Ag <sub>2</sub> O.....	0.8706	9.9398	BaO	BaCO <sub>3</sub> .....	0.7771	9.8905
	Ag <sub>3</sub> PO <sub>4</sub> .....	0.7731	9.8882		BaCrO <sub>4</sub> .....	0.6053	9.7820
	Ag <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	0.7125	9.8528		BaSO <sub>4</sub> .....	0.6570	9.8176
Al	Al <sub>2</sub> O <sub>3</sub> .....	0.5294	9.7238	Ca	CaCl <sub>2</sub> .....	0.3612	9.5577
	AlPO <sub>4</sub> .....	0.2212	9.3449		CaCO <sub>3</sub> .....	0.4005	9.6025
Al <sub>2</sub> O <sub>3</sub>	AlPO <sub>4</sub> .....	0.4179	9.6211		CaF <sub>2</sub> .....	0.5133	9.7103
As	As <sub>2</sub> O <sub>3</sub> .....	0.7575	9.8794		CaO.....	0.7146	9.8541
	As <sub>2</sub> O <sub>5</sub> .....	0.6521	9.8143		CaSO <sub>4</sub> .....	0.2944	9.4689
	As <sub>2</sub> S <sub>3</sub> .....	0.6091	9.7847		CO <sub>2</sub> .....	0.9093	9.9587
	As <sub>2</sub> S <sub>5</sub> .....	0.4832	9.6841	CaO	CaCO <sub>3</sub> .....	0.5603	9.7484
	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub> .....	0.4827	9.6837		CaF <sub>2</sub> .....	0.7182	9.8563
	(NH <sub>4</sub> MgAsO <sub>4</sub> ) <sub>2</sub> , H <sub>2</sub> O.....	0.3939	9.5953		Ca(HCO <sub>3</sub> ) <sub>2</sub> ....	0.3459	9.5389
As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub> .....	0.8609	9.9349		Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ....	0.2394	9.3791
	As <sub>2</sub> S <sub>3</sub> .....	0.8041	9.9053		CaH <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.2594	9.4140
	As <sub>2</sub> S <sub>5</sub> .....	0.6378	9.8047		Ca(HSO <sub>3</sub> ) <sub>2</sub> ....	0.2773	9.4430
	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub> .....	0.6372	9.8043		Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ....	0.5421	9.7341
	(NH <sub>4</sub> MgAsO <sub>4</sub> ) <sub>2</sub> , H <sub>2</sub> O.....	0.5199	9.7160		CaSO <sub>3</sub> .....	0.4667	9.6691
					CaSO <sub>4</sub> .....	0.4120	9.6149
BaCO <sub>3</sub> BaCl <sub>2</sub> ·2H <sub>2</sub> O BaCrO <sub>4</sub> BaF <sub>2</sub> Ba(NO <sub>3</sub> ) <sub>2</sub> Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> BaS	BaSO <sub>4</sub> .....	0.8458	9.9272		CaSO <sub>4</sub> ·2H <sub>2</sub> O...	0.3257	9.5128
	BaSO <sub>4</sub> .....	1.047	0.0198		CO <sub>2</sub> .....	1.274	9.1053
	BaSO <sub>4</sub> .....	1.085	0.0356	Cd	CdO.....	0.8754	9.9422
	BaSiF <sub>6</sub> .....	0.6271	9.7973		CdS.....	0.7780	9.8910
	BaSO <sub>4</sub> .....	1.120	0.0491		CdSO <sub>4</sub> .....	0.6159	9.7895
	BaSO <sub>4</sub> .....	0.8599	9.9245	Bi <sub>2</sub> O <sub>3</sub>	Bi.....	1.115	0.0472
	BaSO <sub>4</sub> .....	0.7258	9.8608		BiOCl.....	0.8946	9.9516
Bi	Bi <sub>2</sub> O <sub>3</sub> .....	0.8970	9.9528		BiPO <sub>4</sub> .....	0.7663	0.8844
	BiOCl.....	0.8024	9.9044		Bi <sub>2</sub> S <sub>3</sub> .....	0.9063	0.9573
	BiPO <sub>4</sub> .....	0.6874	9.8372		BiAsO <sub>4</sub> .....	0.6696	0.8258
	Bi <sub>2</sub> S <sub>3</sub> .....	0.8129	9.9101		BiONO <sub>3</sub> .....	0.8118	9.9095
	BiAsO <sub>4</sub> .....	0.6006	9.7786		Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	0.4803	9.6815
				Br	Ag.....	0.7408	9.8697
As <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> S <sub>3</sub> .....	0.9341	9.9704		AgBr.....	0.4256	9.6290
	As <sub>2</sub> S <sub>5</sub> .....	0.7410	1.8698		AgCl.....	0.5576	9.7463
	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub> .....	0.7403	1.8694		HBr.....	0.9874	9.9945
	(NH <sub>4</sub> MgAsO <sub>4</sub> ) <sub>2</sub> , H <sub>2</sub> O.....	0.6040	9.7810	C	CO <sub>2</sub> .....	0.2727	9.4357
					BaCO <sub>3</sub> .....	0.0608	8.7839
B	B <sub>2</sub> O <sub>3</sub> .....	0.3123	9.4946	Cl	Ag.....	0.3287	9.5168
	KBF <sub>4</sub> .....	0.08651	8.9371		AgCl.....	0.2474	9.3934
	H <sub>3</sub> BO <sub>3</sub> .....	0.1761	9.2456		AgNO <sub>3</sub> .....	0.2088	9.3198
	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.1142	9.0577		HCl.....	0.9724	9.9879

\* From Treadwell-Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons. Reprinted with permission.



## CHEMICAL FACTORS—Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
Cl	I.....	0.2794	9.4462	F	BaSiF <sub>6</sub> .....	0.4076	9.6102
	KCl.....	0.4756	9.6772		CaF <sub>2</sub> .....	0.4866	9.6872
	MnO <sub>2</sub> .....	0.8158	9.9116		CaSO <sub>4</sub> .....	0.2791	9.4457
	NaCl.....	0.6066	9.7829		HF.....	0.9496	9.9776
	NH <sub>4</sub> Cl.....	0.6628	9.8214		H <sub>2</sub> SiF <sub>6</sub> .....	0.7910	9.8982
	RbCl.....	0.2933	9.4673		K <sub>2</sub> SiF <sub>6</sub> .....	0.5170	9.7135
Co	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.2026	9.3066	Fe	NaF.....	0.4524	9.6555
	K <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub> ...	0.1304	9.1152		SiF <sub>4</sub> .....	0.7302	9.8634
	CoO.....	0.7866	9.8957	Fe	Fe <sub>2</sub> O <sub>3</sub> .....	0.6994	9.8447
	Co <sub>3</sub> O <sub>4</sub> .....	0.7344	9.8659		FeCl <sub>2</sub> .....	0.4405	9.6440
	CoSO <sub>4</sub> .....	0.3804	9.5802	HF	BaSiF <sub>6</sub> .....	0.4292	9.6327
	CoSO <sub>4</sub> ·7H <sub>2</sub> O...	0.2097	9.3216		CaF <sub>2</sub> .....	0.5126	9.7098
CoO	Co.....	1.2713	9.1043		CaSO <sub>4</sub> .....	0.2939	9.4682
	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.	0.2575	9.4109		F.....	1.053	0.0224
	K <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub> ...	0.1657	9.2194		K <sub>2</sub> SiF <sub>6</sub> .....	0.5449	9.7363
	Co <sub>3</sub> O <sub>4</sub> .....	0.9336	9.9702	Fe	FeCl <sub>3</sub> ·6H <sub>2</sub> O.....	0.2066	9.3152
	CoSO <sub>4</sub> .....	0.4836	9.6844		Fe(HCO <sub>3</sub> ) <sub>2</sub> .....	0.3140	9.4960
	CoSO <sub>4</sub> ·7H <sub>2</sub> O...	0.2667	9.4259		FeO.....	0.7773	9.8906
Cr	BaCrO <sub>4</sub> .....	0.2052	9.3125		Fe <sub>3</sub> O <sub>4</sub> .....	0.7236	9.8595
	Cr <sub>2</sub> O <sub>3</sub> .....	0.6842	9.8352		FePO <sub>4</sub> .....	0.3701	9.5683
CdO	CdS.....	0.8888	9.9488		FeS.....	0.6352	9.8029
	Cd.....	1.142	0.0578		FeSO <sub>4</sub> .....	0.3676	0.5654
	CdSO <sub>4</sub> .....	0.6159	9.7895		FeSO <sub>4</sub> ·7H <sub>2</sub> O...	0.2008	9.3027
Cr	PbCrO <sub>4</sub> .....	0.1609	9.2067		FeSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O....	0.1424	9.1536
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	0.3535	9.5484		K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (titration)....	1.139	0.0564
	K <sub>2</sub> CrO <sub>4</sub> .....	0.1768	9.2474	FeO	Fe.....	1.287	0.1094
Cr <sub>2</sub> O <sub>3</sub>	BaCrO <sub>4</sub> .....	0.3000	9.4771		FeCO <sub>3</sub> .....	0.6202	9.7925
	PbCrO <sub>4</sub> .....	0.2352	9.3715		Fe(HCO <sub>3</sub> ) <sub>2</sub> .....	0.4039	9.6063
	CrO <sub>3</sub> .....	0.7602	9.8809		Fe <sub>2</sub> O <sub>3</sub> .....	0.8998	9.9542
CrO <sub>4</sub>	BaCrO <sub>4</sub> .....	0.4578	9.6607		FePO <sub>4</sub> .....	0.4761	9.6777
	Cr <sub>2</sub> O <sub>3</sub> .....	1.5263	9.1837		FeS.....	0.8172	9.9123
	PbCrO <sub>4</sub> .....	0.3589	9.5550		FeSO <sub>4</sub> .....	0.4729	9.6747
Cu	Cu <sub>2</sub> O.....	0.8882	9.9485		FeSO <sub>4</sub> ·7H <sub>2</sub> O...	0.2584	9.4123
	CuO.....	0.7989	9.9025		FeSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O....	0.1832	9.2630
	Cu <sub>2</sub> S.....	0.7986	9.9023	Fe <sub>2</sub> O <sub>3</sub>	Fe.....	1.430	0.1553
	Cu <sub>2</sub> (CNS) <sub>2</sub> .....	0.5226	9.7181		FeCl <sub>3</sub> .....	0.4922	9.6922
	CuSO <sub>4</sub> .....	0.3982	9.6001		FeCO <sub>3</sub> .....	0.6892	9.8383
	CuSO <sub>4</sub> ·5H <sub>2</sub> O...	0.2546	9.4058		Fe <sub>3</sub> O <sub>4</sub> .....	1.035	0.0149
CuO	Cu.....	1.252	0.0975		FePO <sub>4</sub> .....	0.5292	9.7237
	Cu <sub>2</sub> O.....	1.113	0.0463		FeS.....	0.9082	9.9582
	Cu <sub>2</sub> S.....	0.9996	9.9998		FeS <sub>2</sub> .....	0.6655	9.8231
	Cu <sub>2</sub> (CNS) <sub>2</sub> .....	0.6541	9.8156		Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	0.3993	9.6013
	CuSO <sub>4</sub> .....	0.4985	9.6976		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O.	0.1656	0.2190
	CuSO <sub>4</sub> ·5H <sub>2</sub> O...	0.3186	9.5032				

## CHEMICAL FACTORS—Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
HBr	Ag.....	0.7505	9.8754	K <sub>2</sub> O	K <sub>2</sub> SO <sub>4</sub> .....	0.5405	9.7328
	AgBr.....	0.4311	9.6346		KClO <sub>4</sub> .....	0.3399	9.5314
HCl	Ag.....	0.3380	9.5290		K <sub>2</sub> PtCl <sub>6</sub> .....	0.1938	9.2873
	AgCl.....	0.2544	9.4056		Pt.....	0.4826	9.6836
	CaCO <sub>3</sub> .....	0.7288	9.8626	KClO <sub>4</sub>	AgCl.....	0.9667	9.9853
	KCl.....	0.4891	9.6894		KCl.....	1.858	0.2691
	K <sub>2</sub> O.....	0.7743	9.8889	H <sub>2</sub> SO <sub>4</sub>	KOH.....	0.8740	9.9415
	NaCl.....	0.6239	9.7951		K <sub>2</sub> SO <sub>4</sub> .....	0.5628	9.7503
	Na <sub>2</sub> O.....	1.176	0.0705		Na <sub>2</sub> CO <sub>3</sub> .....	0.9252	9.9662
	NH <sub>4</sub> Cl.....	0.6817	9.8335		Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	0.7320	9.8645
	SnCl <sub>4</sub> .....	0.5600	9.7480		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	0.7422	9.8705
	Na <sub>2</sub> CO <sub>3</sub> .....	0.6881	9.8377	Hg	Hg <sub>2</sub> Cl <sub>2</sub> .....	0.8495	9.9292
	Methyl orange				HgCl <sub>2</sub> .....	9.7388	9.8686
	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>				HgO.....	0.9261	9.9666
	standardization	0.5442	9.7358		HgS.....	0.8620	9.9355
HI	Ag.....	1.186	0.0742	I	Ag.....	1.177	9.0706
	AgI.....	0.5448	9.7362		AgI.....	0.5406	9.7328
	Pd.....	2.398	0.3799		KI.....	0.7645	9.8834
	PdI <sub>2</sub> .....	0.7097	9.8510		Pd.....	2.379	0.3764
HNO <sub>3</sub>	KNO <sub>3</sub> .....	0.6233	9.7947		PdI <sub>2</sub> .....	0.7041	9.8476
	N.....	4.498	0.6530		Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O.	0.5113	9.7087
	NaNO <sub>3</sub> .....	0.7413	9.8700		AgCl.....	0.8855	9.9472
	NH <sub>3</sub> .....	3.701	0.5683	K	KCl.....	0.5244	9.7197
	NH <sub>4</sub> Cl.....	1.178	0.0711		K <sub>2</sub> O.....	0.8300	9.9191
	(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> ...	0.2838	9.4530		K <sub>2</sub> SO <sub>4</sub> .....	0.4487	9.6520
	NO.....	2.100	0.3222		KClO <sub>4</sub> .....	0.2822	9.4505
	N <sub>2</sub> O <sub>3</sub> .....	0.658	0.2196		K <sub>2</sub> PtCl <sub>6</sub> .....	0.1609	9.2064
	N <sub>2</sub> O <sub>4</sub> .....	1.370	0.1367		Pt.....	0.4006	9.6027
H <sub>3</sub> PO <sub>4</sub>	N <sub>2</sub> O <sub>5</sub> .....	1.167	0.0671	KCl	Ag.....	0.6911	9.8396
	C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> HNO <sub>3</sub>	0.1680	9.2252		AgCl.....	0.5202	9.7162
	Pt.....	0.6457	9.8100		K <sub>2</sub> SO <sub>4</sub> .....	0.8557	9.9323
	HPO <sub>3</sub> .....	1.225	0.0881		KClO <sub>4</sub> .....	0.5381	9.7309
	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	1.101	0.0457		K <sub>2</sub> PtCl <sub>6</sub> .....	0.3067	9.4868
	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.8806	9.9448		Pt.....	0.7640	9.8831
H <sub>2</sub> S	P.....	3.159	0.4995	K <sub>2</sub> O	KCl.....	0.6317	9.8005
	P <sub>2</sub> O <sub>5</sub> .....	1.380	0.1399		MoO <sub>3</sub> .....	0.6667	9.8239
	BaSO <sub>4</sub> .....	0.1460	9.1644	Mo	MoS <sub>3</sub> .....	0.4995	9.6985
	CdS.....	0.2360	9.3729		MoS <sub>2</sub> .....	0.5996	9.7779
H <sub>2</sub> SO <sub>4</sub>	FeS.....	0.3877	9.5885		PbMoO <sub>4</sub> .....	0.2615	9.4174
	S.....	1.063	0.0265		NHNO <sub>3</sub> .....	0.2223	9.3470
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	0.8594	9.9342	N	NO <sub>2</sub> .....	0.3045	9.4835
	Ba(OH) <sub>2</sub> .....	0.5723	9.7576		N <sub>2</sub> O <sub>3</sub> .....	0.3686	9.5665
	BaSO <sub>4</sub> .....	0.4133	9.6163		N <sub>2</sub> O <sub>4</sub> .....	0.3045	9.4835
	K <sub>2</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> · 24H <sub>2</sub> O.....	0.3101	9.4915				
	K <sub>2</sub> O.....	1.041	0.0174				



## CHEMICAL FACTORS—Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
N	N <sub>2</sub> O <sub>5</sub> .....	0.2594	9.4140	NH <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ...	0.2578	9.4113
	NaNO <sub>3</sub> .....	0.1648	9.2169		(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> ...	0.1480	9.1703
	NH <sub>3</sub> .....	0.8225	9.9151		(NH <sub>4</sub> )OH.....	0.4860	9.6866
	Pt.....	0.1435	9.1570		(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> ...	0.07670	8.8848
	NH <sub>4</sub> Cl.....	0.2619	9.4181		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	0.2578	9.4113
K <sub>2</sub> SO <sub>4</sub>	K.....	2.229	0.3481	Na	N <sub>2</sub> O <sub>5</sub> .....	0.3153	9.4987
	KCl.....	1.169	0.0679		Pt.....	0.1745	9.2418
	K <sub>2</sub> O.....	1.850	0.2672		NaCl.....	0.3934	9.5949
	K <sub>2</sub> PtCl <sub>6</sub> .....	0.3585	9.5545		Na <sub>2</sub> SO <sub>4</sub> .....	0.3238	9.5103
	SO <sub>3</sub> .....	2.177	0.3379		NaBr.....	0.2235	9.3493
	BaSO <sub>4</sub> .....	0.7465	9.8731		Na <sub>2</sub> CO <sub>3</sub> .....	0.4340	9.6375
Mg	MgO.....	0.6032	9.7804		NaF.....	0.5476	9.7385
	MgSO <sub>4</sub> .....	0.2020	9.3054		NaHCO <sub>3</sub> .....	0.2740	9.4375
	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.2184	9.3392		NaI.....	0.1534	9.1858
	MgSO <sub>4</sub> .....	0.2020	9.3054		Na <sub>2</sub> O.....	0.7419	9.8704
MgO	MgSO <sub>4</sub> .....	0.3349	9.5249	NaBr	NaOH.....	0.5750	9.7597
	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.3621	9.5588		Na <sub>2</sub> SO <sub>4</sub> .....	0.3238	9.5103
	MgCO <sub>3</sub> .....	0.4782	9.6796		Ag.....	0.9562	9.9806
Mn	MnCO <sub>3</sub> .....	0.4779	9.6793	NaCl	AgBr.....	0.5480	9.7388
	MnO.....	0.7744	9.8889		Ag.....	0.5418	9.7338
	Mn <sub>2</sub> O <sub>3</sub> .....	0.6959	9.8426		AgCl.....	0.4078	9.6105
	Mn <sub>3</sub> O <sub>4</sub> .....	0.7203	9.8575		AgNO <sub>3</sub> .....	0.3441	9.5367
	MnSO <sub>4</sub> .....	0.3638	9.5608	Na <sub>2</sub> HAsO <sub>3</sub>	Na <sub>2</sub> O.....	1.886	0.2756
	Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.3869	9.5876		Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub> .....	1.095	0.0395
	MnS.....	0.6314	9.8003		I.....	0.6697	9.8259
MnO	MnCO <sub>3</sub> .....	0.6172	9.7904	Na <sub>2</sub> HAsO <sub>4</sub>	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub> .....	1.198	0.0785
	Mn <sub>3</sub> O <sub>4</sub> .....	0.9301	9.9685		I.....	0.7328	9.8850
	MnSO <sub>4</sub> .....	0.4697	9.6719	NaHCO <sub>3</sub>	CO <sub>2</sub> .....	1.909	0.2808
	MnS.....	0.8153	9.9113				
	Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.4998	9.6988	NO <sub>3</sub>	NH <sub>4</sub> Cl.....	1.159	0.0641
Na <sub>2</sub> O	NaCl.....	0.5303	9.7245		(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> ...	0.2793	9.4461
	Na <sub>2</sub> SO <sub>4</sub> .....	0.4364	9.6399		Pt.....	0.6354	9.8030
	Na <sub>2</sub> CO <sub>3</sub> .....	0.5849	9.7671		C <sub>20</sub> H <sub>17</sub> N <sub>5</sub> O <sub>3</sub> ...	0.1653	9.2182
	NaHCO <sub>3</sub> .....	0.3690	9.5670	N <sub>2</sub> O <sub>5</sub>	NO.....	1.800	0.2552
	Na <sub>2</sub> HPO <sub>4</sub> .....	0.4365	9.6400		NH <sub>3</sub> .....	3.171	0.5012
	NaH <sub>2</sub> PO <sub>4</sub> .....	0.2582	9.4119		NH <sub>4</sub> Cl.....	1.010	0.0041
	Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.2792	9.4459		(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> ...	0.2433	9.3861
	NaHSO <sub>3</sub> .....	0.2979	9.4741		Pt.....	0.5534	9.7430
	NaNO <sub>3</sub> .....	0.3647	9.5619		C <sub>20</sub> H <sub>17</sub> N <sub>5</sub> O <sub>3</sub> ...	0.1440	9.1582
	NaOH.....	0.7748	9.8891	NO <sub>2</sub>	NO.....	1.533	0.1856
	Na <sub>2</sub> SO <sub>4</sub> .....	0.4364	9.6399				
NH <sub>3</sub>	HNO <sub>3</sub> .....	0.2704	9.4320	P	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.2787	9.4452
	H <sub>2</sub> SO <sub>4</sub> .....	0.3473	9.5407		P <sub>2</sub> O <sub>5</sub> 24MoO <sub>3</sub> ...	0.0173	8.2368
	N.....	1.216	0.0849		(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·		
	NaNO <sub>2</sub> .....	0.2468	9.3923		12MoO <sub>3</sub> .....	0.0165	8.2184
	NaNO <sub>3</sub> .....	0.2005	9.3021		P <sub>2</sub> O <sub>5</sub> .....	0.4369	9.6404
	NH <sub>4</sub> Cl.....	0.3184	9.5023				

## CHEMICAL FACTORS—Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
PO <sub>4</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.8535	9.9312	P <sub>2</sub> O <sub>6</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.6379	9.8048
	P <sub>2</sub> O <sub>5</sub> ·24MoO <sub>3</sub> ..	0.05283	8.7229		P <sub>2</sub> O <sub>5</sub> ·24MoO <sub>3</sub> ..	0.03947	8.5963
	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·				(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·		
	12MoO <sub>3</sub> .....	0.05063	8.7044		12MoO <sub>3</sub> .....	0.03785	8.5780
NH <sub>4</sub>	NH <sub>3</sub> .....	1.059	0.0250	Pb	PbO.....	0.9283	9.9677
	NH <sub>4</sub> Cl.....	0.3372	9.5279		PbO <sub>2</sub> .....	0.8662	9.9376
	(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> ...	0.08125	8.9099		PbS.....	0.8659	9.9375
	Pt.....	0.1848	9.2668		PbSO <sub>4</sub> .....	0.6831	9.8345
Ni	NiO.....	0.7858	9.8953		PbCrO <sub>4</sub> .....	0.6410	9.8068
	NiC <sub>8</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> ..	0.2032	9.3079		PbCl <sub>2</sub> .....	0.7449	9.8721
	NiSO <sub>4</sub> .....	0.3792	9.5788		PbMoO <sub>4</sub> .....	0.5642	9.7515
	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.2018	0.3049	PbO	PbO <sub>2</sub> .....	0.9331	9.9699
	Ni <sub>2</sub> SO <sub>4</sub> ·7H <sub>2</sub> O..	0.2089	9.3200		PbS.....	0.9328	9.9698
S	BaSO <sub>4</sub> .....	0.1374	9.1379		PbSO <sub>4</sub> .....	0.7359	9.8668
	H <sub>2</sub> S.....	0.9408	9.9735		PbCrO <sub>4</sub> .....	0.6905	9.8392
	H <sub>2</sub> SO <sub>4</sub> .....	0.3270	9.5145		PbCl <sub>2</sub> .....	0.8025	9.9044
	FeS.....	0.3648	9.5621		PbCO <sub>3</sub> .....	0.8353	9.9219
	FeS <sub>2</sub> .....	0.5346	9.7280		Pb(NO <sub>3</sub> ) <sub>2</sub> .....	0.6738	9.8285
	Na <sub>2</sub> S.....	0.4108	9.6136	Sn	SnO <sub>2</sub> .....	0.7881	9.8966
SO <sub>2</sub>	BaSO <sub>4</sub> .....	0.2745	9.4385		SnO.....	0.8812	9.9451
	S.....	1.998	0.3007		SnCl <sub>2</sub> .....	0.6261	9.7967
SO <sub>3</sub>	BaSO <sub>4</sub> .....	0.3430	9.5353		SnCl <sub>2</sub> ·2H <sub>2</sub> O....	0.5260	9.7210
	CaSO <sub>4</sub> .....	0.5881	9.7695	Sr	SrO.....	0.8456	9.9272
	H <sub>2</sub> SO <sub>4</sub> .....	0.8163	9.9119		SrCO <sub>3</sub> .....	0.5936	9.7735
	K <sub>2</sub> SO <sub>4</sub> .....	0.4595	9.6623		SrSO <sub>4</sub> .....	0.4770	9.6785
	Na <sub>2</sub> SO <sub>4</sub> .....	0.5636	9.7510		Sr(NO <sub>3</sub> ) <sub>2</sub> .....	0.4140	9.6170
SO <sub>4</sub>	BaSO <sub>4</sub> .....	0.4115	9.6144	SrO	SrCO <sub>3</sub> .....	0.7020	9.8463
					SrSO <sub>4</sub> .....	0.5641	9.7514
Sb	KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·				Sr(NO <sub>3</sub> ) <sub>2</sub> .....	0.4896	9.6899
	$\frac{1}{2}$ H <sub>2</sub> O.....	0.3648	9.5620	Ti	TiCl.....	0.8519	9.9304
	SbCl <sub>3</sub> .....	0.5339	9.7275		Ti <sub>2</sub> CO <sub>3</sub> .....	0.8718	9.9404
	Sb <sub>2</sub> O <sub>3</sub> .....	0.8356	9.9220		TiI.....	0.6165	9.7900
	Sb <sub>2</sub> O <sub>5</sub> .....	0.7528	9.8767	V	V <sub>2</sub> O <sub>5</sub> .....	0.5605	9.7485
	Sb <sub>2</sub> O <sub>4</sub> .....	0.7921	9.8988		V <sub>2</sub> O <sub>4</sub> .....	0.6144	9.7885
	Sb <sub>2</sub> S <sub>3</sub> .....	0.7169	9.8555	W	WO <sub>3</sub> .....	0.7931	9.8993
	Sb <sub>2</sub> S <sub>5</sub> .....	0.6030	9.7803		PbWO <sub>4</sub> .....	0.4435	9.6469
Si	SiO <sub>2</sub> .....	0.4676	9.6698	Zn	ZnO.....	0.8034	9.9049
	SiO <sub>3</sub> .....	0.3693	9.5673		ZnNH <sub>4</sub> PO <sub>4</sub> ....	0.3663	9.5639
	SiO <sub>4</sub> .....	0.3051	9.4844		Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.4290	9.6324
U	U <sub>3</sub> O <sub>8</sub> .....	0.8482	9.9285		ZnS.....	0.6709	9.8266
	UO <sub>2</sub> .....	0.8817	9.9453	ZnO	ZnS.....	0.8351	9.9217
	(UO <sub>2</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ....	0.6670	9.8242		ZnNH <sub>4</sub> PO <sub>4</sub> ....	0.4561	9.6590
					Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.5340	9.7275



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts			
100	00 000	043	087	130	173	217	260	303	346	389				
01	432	475	518	561	604	647	689	732	775	817				
02	00 860	903	945	988	*030	*072	*115	*157	*199	*242	44	43	42	
03	01 284	326	368	410	452	494	536	578	620	662	1	4.4	4.3	4.2
											2	8.8	8.6	8.4
04	01 703	745	787	828	870	912	953	995	*036	*078	3	13.2	12.9	12.6
05	02 119	160	202	243	284	325	366	407	449	490	4	17.6	17.2	16.8
06	531	572	612	653	694	735	776	816	857	898	5	22.0	21.5	21.0
											6	26.4	25.8	25.2
07	02 938	979	*019	*060	*100	*141	*181	*222	*262	*302	7	30.8	30.1	29.4
08	03 342	383	423	463	503	543	583	623	663	703	8	35.2	34.4	33.6
09	03 743	782	822	862	902	941	981	*021	*060	*100	9	39.6	38.7	37.8
110	04 139	179	218	258	297	336	376	415	454	493				
11	532	571	610	650	689	727	766	805	844	883				
12	04 922	961	999	*038	*077	*115	*154	*192	*231	*269	41	40	39	
13	05 308	346	385	423	461	500	538	576	614	652	1	4.1	4	3.9
											2	8.2	8	7.8
14	05 690	729	767	805	843	881	918	956	994	*032	3	12.3	12	11.7
15	06 070	108	145	183	221	258	296	333	371	408	4	16.4	16	15.6
16	446	483	521	558	595	633	670	707	744	781	5	20.5	20	19.5
											6	24.6	24	23.4
17	06 819	856	893	930	967	*004	*041	*078	*115	*151	7	28.7	28	27.3
18	07 188	225	262	298	335	372	408	445	482	518	8	32.8	32	31.2
19	555	591	628	664	700	737	773	809	846	882	9	36.9	36	35.1
120	07 918	954	990	*027	*063	*099	*135	*171	*207	*243				
21	08 279	314	350	386	422	458	493	529	565	600				
22	636	672	707	743	778	814	849	884	920	955	38	37	36	
23	08 991	*026	*061	*096	*132	*167	*202	*237	*272	*307	1	3.8	3.7	3.6
											2	7.6	7.4	7.2
24	09 342	377	412	447	482	517	552	587	621	656	3	11.4	11.1	10.8
25	09 691	726	760	795	830	864	899	934	968	*003	4	15.2	14.8	14.4
26	10 037	072	106	140	175	209	243	278	312	346	5	19.0	18.5	18.0
											6	22.8	22.2	21.6
27	380	415	449	483	517	551	585	619	653	687	7	26.6	25.9	25.2
28	10 721	755	789	823	857	890	924	958	992	*025	8	30.4	29.6	28.8
29	11 059	093	126	160	193	227	261	294	327	361	9	34.2	33.3	32.4
130	394	428	461	494	528	561	594	628	661	694				
31	11 727	760	793	826	860	893	926	959	992	*024				
32	12 057	090	123	156	189	222	254	287	320	352	35	34	33	
33	385	418	450	483	516	548	581	613	646	678	1	3.5	3.4	3.3
											2	7.0	6.8	6.6
34	12 710	743	775	808	840	872	905	937	969	*001	3	10.5	10.2	9.9
35	13 033	066	098	130	162	194	226	258	290	322	4	14.0	13.6	13.2
36	354	386	418	450	481	513	545	577	609	640	5	17.5	17.0	16.5
											6	21.0	20.4	19.8
37	672	704	735	767	799	830	862	893	925	956	7	24.5	23.8	23.1
38	13 988	*019	*051	*082	*114	*145	*176	*208	*239	*270	8	28.0	27.2	26.4
39	14 301	333	364	395	426	457	489	520	551	582	9	31.5	30.6	29.7
140	613	644	675	706	737	768	799	829	860	891				
41	14 922	953	983	*014	*045	*076	*106	*137	*168	*198				
42	15 229	259	290	320	351	381	412	442	473	503	32	31	30	
43	534	564	594	625	655	685	715	746	776	806	1	3.2	3.1	3
											2	6.4	6.2	6
44	15 836	866	897	927	957	987	*017	*047	*077	*107	3	9.6	9.3	9
45	16 137	167	197	227	256	286	316	346	376	406	4	12.8	12.4	12
46	435	465	495	524	554	584	613	643	673	702	5	16.0	15.5	15
											6	19.2	18.6	18
47	16 732	761	791	820	850	879	909	938	967	997	7	22.4	21.7	21
48	17 026	056	085	114	143	173	202	231	260	289	8	25.6	24.8	24
49	319	348	377	406	435	464	493	522	551	580	9	28.8	27.9	27
150	17 609	638	667	696	725	754	782	811	840	869				
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts			



Prop. Parts			N	0	1	2	3	4	5	6	7	8	9
			150	17 609	638	667	696	725	754	782	811	840	869
1 2 3 4 5 6 7 8 9	29 28 2.9 2.8 5.8 5.6 8.7 8.4 11.6 11.2 14.5 14.0 17.4 16.8 20.3 19.6 23.2 22.4 26.1 25.2		51	17 898	926	955	984	*013	*041	*070	*099	*127	*156
			52	18 184	213	241	270	298	327	355	384	412	441
			53	469	498	526	554	583	611	639	667	696	724
			54	18 752	780	808	837	865	893	921	949	977	*005
			55	19 033	061	089	117	145	173	201	229	257	285
			56	312	340	368	396	424	451	479	507	535	562
			57	590	618	645	673	700	728	756	783	811	838
			58	19 866	893	921	948	976	*003	*030	*058	*085	*112
			59	20 140	167	194	222	249	276	303	330	358	385
			160	412	439	466	493	520	548	575	602	629	656
1 2 3 4 5 6 7 8 9	27 26 2.7 2.6 5.4 5.2 8.1 7.8 10.8 10.4 13.5 13.0 16.2 15.6 18.9 18.2 21.6 20.8 24.3 23.4		61	683	710	737	763	790	817	844	871	898	925
			62	20 952	978	*005	*032	*059	*085	*112	*139	*165	*192
			63	21 219	245	272	299	325	352	378	405	431	458
			64	484	511	537	564	590	617	643	669	696	722
			65	21 748	775	801	827	854	880	906	932	958	985
			66	22 011	037	063	089	115	141	167	194	220	246
			67	272	298	324	350	376	401	427	453	479	505
			68	531	557	583	608	634	660	686	712	737	763
			69	22 789	814	840	866	891	917	943	968	994	*019
			170	23 045	070	096	121	147	172	198	223	249	274
1 2 3 4 5 6 7 8 9	25 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5		71	300	325	350	376	401	426	452	477	502	528
			72	553	578	603	629	654	679	704	729	754	779
			73	23 805	830	855	880	905	930	955	980	*005	*030
			74	24 055	080	105	130	155	180	204	229	254	279
			75	304	329	353	378	403	428	452	477	502	527
			76	551	576	601	625	650	674	699	724	748	773
			77	24 797	822	846	871	895	920	944	969	993	*018
			78	25 042	066	091	115	139	164	188	212	237	261
			79	285	310	334	358	382	406	431	455	479	503
			180	527	551	575	600	624	648	672	696	720	744
1 2 3 4 5 6 7 8 9	24 23 2.4 2.3 4.8 4.6 7.2 6.9 9.6 9.2 12.0 11.5 14.4 13.8 16.8 16.1 19.2 18.4 21.6 20.7		81	25 768	792	816	840	864	888	912	935	959	983
			82	26 007	031	055	079	102	126	150	174	198	221
			83	245	269	293	316	340	364	387	411	435	458
			84	482	505	529	553	576	600	623	647	670	694
			85	717	741	764	788	811	834	858	881	905	928
			86	26 951	975	998	*021	*045	*068	*091	*114	*138	*161
			87	27 184	207	231	254	277	300	323	346	370	393
			88	416	439	462	485	508	531	554	577	600	623
			89	646	669	692	715	738	761	784	807	830	852
			190	27 875	898	921	944	967	989	*012	*035	*058	*081
1 2 3 4 5 6 7 8 9	22 21 2.2 2.1 4.4 4.2 6.6 6.3 8.8 8.4 11.0 10.5 13.2 12.6 15.4 14.7 17.6 16.8 19.8 18.9		91	28 103	126	149	171	194	217	240	262	285	307
			92	330	353	375	398	421	443	466	488	511	533
			93	556	578	601	623	646	668	691	713	735	758
			94	28 780	803	825	847	870	892	914	937	959	981
			95	29 003	026	048	070	092	115	137	159	181	203
			96	226	248	270	292	314	336	358	380	403	425
			97	447	469	491	513	535	557	579	601	623	645
			98	667	688	710	732	754	776	798	820	842	863
			99	29 885	907	929	951	973	994	*016	*038	*060	*081
			200	30 103	125	146	168	190	211	233	255	276	298
Prop. Parts			N	0	1	2	3	4	5	6	7	8	9



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
200	30 103	125	146	168	190	211	233	255	276	298	
01	320	341	363	384	406	428	449	471	492	514	
02	535	557	578	600	621	643	664	685	707	728	
03	750	771	792	814	835	856	878	899	920	942	
04	30 963	984	*006	*027	*048	*069	*091	*112	*133	*154	
05	31 175	197	218	239	260	281	302	323	345	366	
06	387	408	429	450	471	492	513	534	555	576	
07	597	618	639	660	681	702	723	744	765	785	
08	31 806	827	848	869	890	911	931	952	973	994	
09	32 015	035	056	077	098	118	139	160	181	201	
210	222	243	263	284	305	325	346	366	387	408	
11	428	449	469	490	510	531	552	572	593	613	
12	634	654	675	695	715	736	756	777	797	818	
13	32 838	858	879	899	919	940	960	980	*001	*021	
14	33 041	062	082	102	122	143	163	183	203	224	
15	244	264	284	304	325	345	365	385	405	425	
16	445	465	486	506	526	546	566	586	606	626	
17	646	666	686	706	726	746	766	786	806	826	
18	33 846	866	885	905	925	945	965	985	*005	*025	
19	34 044	064	084	104	124	143	163	183	203	223	
220	242	262	282	301	321	341	361	380	400	420	
21	439	459	479	498	518	537	557	577	596	616	
22	635	655	674	694	713	733	753	772	792	811	
23	34 830	850	869	889	908	928	947	967	986	*005	
24	35 025	044	064	083	102	122	141	160	180	199	
25	218	238	257	276	295	315	334	353	372	392	
26	411	430	449	468	488	507	526	545	564	583	
27	603	622	641	660	679	698	717	736	755	774	
28	793	813	832	851	870	889	908	927	946	965	
29	35 984	*003	*021	*040	*059	*078	*097	*116	*135	*154	
230	36 173	192	211	229	248	267	286	305	324	342	
31	361	380	399	418	436	455	474	493	511	530	
32	549	568	586	605	624	642	661	680	698	717	
33	736	754	773	791	810	829	847	866	884	903	
34	36 922	940	959	977	996	*014	*033	*051	*070	*088	
35	37 107	125	144	162	181	199	218	236	254	273	
36	291	310	328	346	365	383	401	420	438	457	
37	475	493	511	530	548	566	585	603	621	639	
38	658	676	694	712	731	749	767	785	803	822	
39	37 840	858	876	894	912	931	949	967	985	*003	
240	38 021	039	057	075	093	112	130	148	166	184	
41	202	220	238	256	274	292	310	328	346	364	
42	382	399	417	435	453	471	489	507	525	543	
43	561	578	596	614	632	650	668	686	703	721	
44	739	757	775	792	810	828	846	863	881	899	
45	38 917	934	952	970	987	*005	*023	*041	*058	*076	
46	39 094	111	129	146	164	182	199	217	235	252	
47	270	287	305	322	340	358	375	393	410	428	
48	445	463	480	498	515	533	550	568	585	602	
49	620	637	655	672	690	707	724	742	759	777	
250	39 794	811	829	846	863	881	898	915	933	950	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

	22	21
1	2.2	2.1
2	4.4	4.2
3	6.6	6.3
4	8.8	8.4
5	11.0	10.5
6	13.2	12.6
7	15.4	14.7
8	17.6	16.8
9	19.8	18.9

	20
1	2
2	4
3	6
4	8
5	10
6	12
7	14
8	16
9	18

	19
1	1.9
2	3.8
3	5.7
4	7.6
5	9.5
6	11.4
7	13.3
8	15.2
9	17.1

	18
1	1.8
2	3.6
3	5.4
4	7.2
5	9.0
6	10.8
7	12.6
8	14.4
9	16.2

	17
1	1.7
2	3.4
3	5.1
4	6.8
5	8.5
6	10.2
7	11.9
8	13.6
9	15.3



Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		250	39 794	811	829	846	863	881	898	915	933	950
18 1 1.8 2 3.6 3 5.4 4 7.2 5 9.0 6 10.8 7 12.6 8 14.4 9 16.2		51	39 967	985	*002	*019	*037	*054	*071	*088	*106	*123
		52	40 140	157	175	192	209	226	243	261	278	295
		53	312	329	346	364	381	398	415	432	449	466
		54	483	500	518	535	552	569	586	603	620	637
		55	654	671	688	705	722	739	756	773	790	807
		56	824	841	858	875	892	909	926	943	960	976
		57	40 993	*010	*027	*044	*061	*078	*095	*111	*128	*145
		58	41 162	179	196	212	229	246	263	280	296	313
		59	330	347	363	380	397	414	430	447	464	481
		260	497	514	531	547	564	581	597	614	631	647
17 1 1.7 2 3.4 3 5.1 4 6.8 5 8.5 6 10.2 7 11.9 8 13.6 9 15.3		61	664	681	697	714	731	747	764	780	797	814
		62	830	847	863	880	896	913	929	946	963	979
		63	41 996	*012	*029	*045	*062	*078	*095	*111	*127	*144
		64	42 160	177	193	210	226	243	259	275	292	308
		65	325	341	357	374	390	406	423	439	455	472
		66	488	504	521	537	553	570	586	602	619	635
		67	651	667	684	700	716	732	749	765	781	797
		68	813	830	846	862	878	894	911	927	943	959
		69	42 975	991	*008	*024	*040	*056	*072	*088	*104	*120
		270	43 136	152	169	185	201	217	233	249	265	281
16 1 1.6 2 3.2 3 4.8 4 6.4 5 8.0 6 9.6 7 11.2 8 12.8 9 14.4		71	297	313	329	345	361	377	393	409	425	441
		72	457	473	489	505	521	537	553	569	584	600
		73	616	632	648	664	680	696	712	727	743	759
		74	775	791	807	823	838	854	870	886	902	917
		75	43 933	949	965	981	996	*012	*028	*044	*059	*075
		76	44 091	107	122	138	154	170	185	201	217	232
		77	248	264	279	295	311	326	342	358	373	389
		78	404	420	436	451	467	483	498	514	529	545
		79	560	576	592	607	623	638	654	669	685	700
		280	716	731	747	762	778	793	809	824	840	855
15 1 1.5 2 3.0 3 4.5 4 6.0 5 7.5 6 9.0 7 10.5 8 12.0 9 13.5		81	44 871	886	902	917	932	948	963	979	994	*010
		82	45 025	040	056	071	086	102	117	133	148	163
		83	179	194	209	225	240	255	271	286	301	317
		84	332	347	362	378	393	408	423	439	454	469
		85	484	500	515	530	545	561	576	591	606	621
		86	637	652	667	682	697	712	728	743	758	773
		87	788	803	818	834	849	864	879	894	909	924
		88	45 939	954	969	984	*000	*015	*030	*045	*060	*075
		89	46 090	105	120	135	150	165	180	195	210	225
		290	240	255	270	285	300	315	330	345	359	374
14 1 1.4 2 2.8 3 4.2 4 5.6 5 7.0 6 8.4 7 9.8 8 11.2 9 12.6		91	389	404	419	434	449	464	479	494	509	523
		92	538	553	568	583	598	613	627	642	657	672
		93	687	702	716	731	746	761	776	790	805	820
		94	835	850	864	879	894	909	923	938	953	967
		95	46 982	997	*012	*026	*041	*056	*070	*085	*100	*114
		96	47 129	144	159	173	188	202	217	232	246	261
		97	276	290	305	319	334	349	363	378	392	407
		98	422	436	451	465	480	494	509	524	538	553
		99	567	582	596	611	625	640	654	669	683	698
		300	47 712	727	741	756	770	784	799	813	828	842
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
300	47 712	727	741	756	770	784	799	813	828	842	
01	47 857	871	885	900	914	929	943	958	972	986	
02	48 001	015	029	044	058	073	087	101	116	130	
03	144	159	173	187	202	216	230	244	259	273	
04	287	302	316	330	344	359	373	387	401	416	
05	430	444	458	473	487	501	515	530	544	558	
06	572	586	601	615	629	643	657	671	686	700	
07	714	728	742	756	770	785	799	813	827	841	
08	855	869	883	897	911	926	940	954	968	982	
09	48 996	*010	*024	*038	*052	*066	*080	*094	*108	*122	
310	49 136	150	164	178	192	206	220	234	248	262	
11	276	290	304	318	332	346	360	374	388	402	
12	415	429	443	457	471	485	499	513	527	541	
13	554	568	582	596	610	624	638	651	665	679	
14	693	707	721	734	748	762	776	790	803	817	
15	831	845	859	872	886	900	914	927	941	955	
16	49 969	982	996	*010	*024	*037	*051	*065	*079	*092	
17	50 106	120	133	147	161	174	188	202	215	229	
18	243	256	270	284	297	311	325	338	352	365	
19	379	393	406	420	433	447	461	474	488	501	
320	515	529	542	556	569	583	596	610	623	637	
21	651	664	678	691	705	718	732	745	759	772	
22	786	799	813	826	840	853	866	880	893	907	
23	50 920	934	947	961	974	987	*001	*014	*028	*041	
24	51 055	068	081	095	108	121	135	148	162	175	
25	188	202	215	228	242	255	268	282	295	308	
26	322	335	348	362	375	388	402	415	428	441	
27	455	468	481	495	508	521	534	548	561	574	
28	587	601	614	627	640	654	667	680	693	706	
29	720	733	746	759	772	786	799	812	825	838	
330	851	865	878	891	904	917	930	943	957	970	
31	51 983	996	*009	*022	*035	*048	*061	*075	*088	*101	
32	52 114	127	140	153	166	179	192	205	218	231	
33	244	257	270	284	297	310	323	336	349	362	
34	375	388	401	414	427	440	453	466	479	492	
35	504	517	530	543	556	569	582	595	608	621	
36	634	647	660	673	686	699	711	724	737	750	
37	763	776	789	802	815	827	840	853	866	879	
38	52 892	905	917	930	943	956	969	982	994	*007	
39	53 020	033	046	058	071	084	097	110	122	135	
340	148	161	173	186	199	212	224	237	250	263	
41	275	288	301	314	326	339	352	364	377	390	
42	403	415	428	441	453	466	479	491	504	517	
43	529	542	555	567	580	593	605	618	631	643	
44	656	668	681	694	706	719	732	744	757	769	
45	782	794	807	820	832	845	857	870	882	895	
46	53 908	920	933	945	958	970	983	995	*008	*020	
47	54 033	045	058	070	083	095	108	120	133	145	
48	158	170	183	195	208	220	233	245	258	270	
49	283	295	307	320	332	345	357	370	382	394	
350	54 407	419	432	444	456	469	481	494	506	518	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

	15
1	1.5
2	3.0
3	4.5
4	6.0
5	7.5
6	9.0
7	10.5
8	12.0
9	13.5

	14
1	1.4
2	2.8
3	4.2
4	5.6
5	7.0
6	8.4
7	9.8
8	11.2
9	12.6

	13
1	1.3
2	2.6
3	3.9
4	5.2
5	6.5
6	7.8
7	9.1
8	10.4
9	11.7

	12
1	1.2
2	2.4
3	3.6
4	4.8
5	6.0
6	7.2
7	8.4
8	9.6
9	10.8

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		350	54 407	419	432	444	456	469	481	494	506	518
		51	531	543	555	568	580	593	605	617	630	642
		52	654	667	679	691	704	716	728	741	753	765
		53	777	790	802	814	827	839	851	864	876	888
<b>13</b>												
1	1.3	54	54 900	913	925	937	949	962	974	986	998	*011
2	2.6	55	55 023	035	047	060	072	084	096	108	121	133
3	3.9	56	145	157	169	182	194	206	218	230	242	255
4	5.2											
5	6.5											
6	7.8	57	267	279	291	303	315	328	340	352	364	376
7	9.1	58	388	400	413	425	437	449	461	473	485	497
8	10.4	59	509	522	534	546	558	570	582	594	606	618
9	11.7											
		360	630	642	654	666	678	691	703	715	727	739
		61	751	763	775	787	799	811	823	835	847	859
		62	871	883	895	907	919	931	943	955	967	979
		63	55 991	*003	*015	*027	*038	*050	*062	*074	*086	*098
		64	56 110	122	134	146	158	170	182	194	205	217
		65	229	241	253	265	277	289	301	312	324	336
		66	348	360	372	384	396	407	419	431	443	455
<b>12</b>												
1	1.2	67	467	478	490	502	514	526	538	549	561	573
2	2.4	68	585	597	608	620	632	644	656	667	679	691
3	3.6	69	703	714	726	738	750	761	773	785	797	808
4	4.8											
5	6.0											
6	7.2											
7	8.4											
8	9.6											
9	10.8											
		370	820	832	844	855	867	879	891	902	914	926
		71	56 937	949	961	972	984	996	*008	*019	*031	*043
		72	57 054	066	078	089	101	113	124	136	148	159
		73	171	183	194	206	217	229	241	252	264	276
		74	287	299	310	322	334	345	357	368	380	392
		75	403	415	426	438	449	461	473	484	496	507
		76	519	530	542	553	565	576	588	600	611	623
		77	634	646	657	669	680	692	703	715	726	738
		78	749	761	772	784	795	807	818	830	841	852
		79	864	875	887	898	910	921	933	944	955	967
<b>11</b>												
1	1.1											
2	2.2											
3	3.3	380	57 978	990	*001	*013	*024	*035	*047	*058	*070	*081
4	4.4											
5	5.5	81	58 092	104	115	127	138	149	161	172	184	195
6	6.6	82	206	218	229	240	252	263	274	286	297	309
7	7.7	83	320	331	343	354	365	377	388	399	410	422
8	8.8											
9	9.9	84	433	444	456	467	478	490	501	512	524	535
		85	546	557	569	580	591	602	614	625	636	647
		86	659	670	681	692	704	715	726	737	749	760
		87	771	782	794	805	816	827	838	850	861	872
		88	883	894	906	917	928	939	950	961	973	984
		89	58 995	*006	*017	*028	*040	*051	*062	*073	*084	*095
		390	59 106	118	129	140	151	162	173	184	195	207
<b>10</b>												
1	1.0	91	218	229	240	251	262	273	284	295	306	318
2	2.0	92	329	340	351	362	373	384	395	406	417	428
3	3.0	93	439	450	461	472	483	494	506	517	528	539
4	4.0											
5	5.0	94	550	561	572	583	594	605	616	627	638	649
6	6.0	95	660	671	682	693	704	715	726	737	748	759
7	7.0	96	770	780	791	802	813	824	835	846	857	868
8	8.0											
9	9.0	97	879	890	901	912	923	934	945	956	966	977
		98	59 988	999	*010	*021	*032	*043	*054	*065	*076	*086
		99	60 097	108	119	130	141	152	163	173	184	195
		400	60 206	217	228	239	249	260	271	282	293	304
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
400	60 206	217	228	239	249	260	271	282	293	304	
01	314	325	336	347	358	369	379	390	401	412	
02	423	433	444	455	466	477	487	498	509	520	
03	531	541	552	563	574	584	595	606	617	627	
04	638	649	660	670	681	692	703	713	724	735	
05	746	756	767	778	788	799	810	821	831	842	
06	853	863	874	885	895	906	917	927	938	949	
07	60 959	970	981	991	*002	*013	*023	*034	*045	*055	
08	61 066	077	087	098	109	119	130	140	151	162	
09	172	183	194	204	215	225	236	247	257	268	
410	278	289	300	310	321	331	342	352	363	374	
11	384	395	405	416	426	437	448	458	469	479	
12	490	500	511	521	532	542	553	563	574	584	
13	595	606	616	627	637	648	658	669	679	690	
14	700	711	721	731	742	752	763	773	784	794	
15	805	815	826	836	847	857	868	878	888	899	
16	61 909	920	930	941	951	962	972	982	993	*003	
17	62 014	024	034	045	055	066	076	086	097	107	
18	118	128	138	149	159	170	180	190	201	211	
19	221	232	242	252	263	273	284	294	304	315	
420	325	335	346	356	366	377	387	397	408	418	
21	428	439	449	459	469	480	490	500	511	521	
22	531	542	552	562	572	583	593	603	613	624	
23	634	644	655	665	675	685	696	706	716	726	
24	737	747	757	767	778	788	798	808	818	829	
25	839	849	859	870	880	890	900	910	921	931	
26	62 941	951	961	972	982	992	*002	*012	*022	*033	
27	63 043	053	063	073	083	094	104	114	124	134	
28	144	155	165	175	185	195	205	215	225	236	
29	246	256	266	276	286	296	306	317	327	337	
430	347	357	367	377	387	397	407	417	428	438	
31	448	458	468	478	488	498	508	518	528	538	
32	548	558	568	579	589	599	609	619	629	639	
33	649	659	669	679	689	699	709	719	729	739	
34	749	759	769	779	789	799	809	819	829	839	
35	849	859	869	879	889	899	909	919	929	939	
36	63 949	959	969	979	988	998	*008	*018	*028	*038	
37	64 048	058	068	078	088	098	108	118	128	137	
38	147	157	167	177	187	197	207	217	227	237	
39	246	256	266	276	286	296	306	316	326	335	
440	345	355	365	375	385	395	404	414	424	434	
41	444	454	464	473	483	493	503	513	523	532	
42	542	552	562	572	582	591	601	611	621	631	
43	640	650	660	670	680	689	699	709	719	729	
44	738	748	758	768	777	787	797	807	816	826	
45	836	846	856	865	875	885	895	904	914	924	
46	64 933	943	953	963	972	982	992	*002	*011	*021	
47	65 031	040	050	060	070	079	089	099	108	118	
48	128	137	147	157	167	176	186	196	205	215	
49	225	234	244	254	263	273	283	292	302	312	
450	65 321	331	341	350	360	369	379	389	398	408	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

11

1 1.1  
2 2.2  
3 3.3  
4 4.4  
5 5.5  
6 6.6  
7 7.7  
8 8.8  
9 9.9

10

1 1.0  
2 2.0  
3 3.0  
4 4.0  
5 5.0  
6 6.0  
7 7.0  
8 8.0  
9 9.0

9

1 0.9  
2 1.8  
3 2.7  
4 3.6  
5 4.5  
6 5.4  
7 6.3  
8 7.2  
9 8.1

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		450	65 321	331	341	350	360	369	379	389	398	408
		51	418	427	437	447	456	466	475	485	495	504
		52	514	523	533	543	552	562	571	581	591	600
		53	610	619	629	639	648	658	667	677	686	696
		54	706	715	725	734	744	753	763	772	782	792
		55	801	811	820	830	839	849	858	868	877	887
		56	896	906	916	925	935	944	954	963	973	982
10 1 1.0 2 2.0 3 3.0 4 4.0 5 5.0 6 6.0 7 7.0 8 8.0 9 9.0		57	65 992	*001	*011	*020	*030	*039	*049	*058	*068	*077
		58	66 087	096	106	115	124	134	143	153	162	172
		59	181	191	200	210	219	229	238	247	257	266
		460	276	285	295	304	314	323	332	342	351	361
		61	370	380	389	398	408	417	427	436	445	455
		62	464	474	483	492	502	511	521	530	539	549
		63	558	567	577	586	596	605	614	624	633	642
		64	652	661	671	680	689	699	708	717	727	736
		65	745	755	764	773	783	792	801	811	820	829
		66	839	848	857	867	876	885	894	904	913	922
		67	66 932	941	950	960	969	978	987	997	*006	*015
		68	67 025	034	043	052	062	071	080	089	099	108
		69	117	127	136	145	154	164	173	182	191	201
		470	210	219	228	237	247	256	265	274	284	293
9 1 0.9 2 1.8 3 2.7 4 3.6 5 4.5 6 5.4 7 6.3 8 7.2 9 8.1		71	302	311	321	330	339	348	357	367	376	385
		72	394	403	413	422	431	440	449	459	468	477
		73	486	495	504	514	523	532	541	550	560	569
		74	578	587	596	605	614	624	633	642	651	660
		75	669	679	688	697	706	715	724	733	742	752
		76	761	770	779	788	797	806	815	825	834	843
		77	852	861	870	879	888	897	906	916	925	934
		78	67 943	952	961	970	979	988	997	*006	*015	*024
		79	68 034	043	052	061	070	079	088	097	106	115
		480	124	133	142	151	160	169	178	187	196	205
		81	215	224	233	242	251	260	269	278	287	296
		82	305	314	323	332	341	350	359	368	377	386
		83	395	404	413	422	431	440	449	458	467	476
		84	485	494	502	511	520	529	538	547	556	565
		85	574	583	592	601	610	619	628	637	646	655
		86	664	673	681	690	699	708	717	726	735	744
		87	753	762	771	780	789	797	806	815	824	833
		88	842	851	860	869	878	886	895	904	913	922
		89	68 931	940	949	958	966	975	984	993	*002	*011
		490	69 020	028	037	046	055	064	073	082	090	099
8 1 0.8 2 1.6 3 2.4 4 3.2 5 4.0 6 4.8 7 5.6 8 6.4 9 7.2		91	108	117	126	135	144	152	161	170	179	188
		92	197	205	214	223	232	241	249	258	267	276
		93	285	294	302	311	320	329	338	346	355	364
		94	373	381	390	399	408	417	425	434	443	452
		95	461	469	478	487	496	504	513	522	531	539
		96	548	557	566	574	583	592	601	609	618	627
		97	636	644	653	662	671	679	688	697	705	714
		98	723	732	740	749	758	767	775	784	793	801
		99	810	819	827	836	845	854	862	871	880	888
		500	69 897	906	914	923	932	940	949	958	966	975
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
500	69 897	906	914	923	932	940	949	958	966	975	
01	69 984	992	*001	*010	*018	*027	*036	*044	*053	*062	
02	70 070	079	088	096	105	114	122	131	140	148	
03	157	165	174	183	191	200	209	217	226	234	
04	243	252	260	269	278	286	295	303	312	321	
05	329	338	346	355	364	372	381	389	398	406	
06	415	424	432	441	449	458	467	475	484	492	
07	501	509	518	526	535	544	552	561	569	578	
08	586	595	603	612	621	629	638	646	655	663	
09	672	680	689	697	706	714	723	731	740	749	
510	757	766	774	783	791	800	808	817	825	834	
11	842	851	859	868	876	885	893	902	910	919	
12	70 927	935	944	952	961	969	978	986	995	*003	
13	71 012	020	029	037	046	054	063	071	079	088	
14	096	105	113	122	130	139	147	155	164	172	
15	181	189	198	206	214	223	231	240	248	257	
16	265	273	282	290	299	307	315	324	332	341	
17	349	357	366	374	383	391	399	408	416	425	
18	433	441	450	458	466	475	483	492	500	508	
19	517	525	533	542	550	559	567	575	584	592	
520	600	609	617	625	634	642	650	659	667	675	
21	684	692	700	709	717	725	734	742	750	759	
22	767	775	784	792	800	809	817	825	834	842	
23	850	858	867	875	883	892	900	908	917	925	
24	71 933	941	950	958	966	975	983	991	999	*008	
25	72 016	024	032	041	049	057	066	074	082	090	
26	099	107	115	123	132	140	148	156	165	173	
27	181	189	198	206	214	222	230	239	247	255	
28	263	272	280	288	296	304	313	321	329	337	
29	346	354	362	370	378	387	395	403	411	419	
530	428	436	444	452	460	469	477	485	493	501	
31	509	518	526	534	542	550	558	567	575	583	
32	591	599	607	616	624	632	640	648	656	665	
33	673	681	689	697	705	713	722	730	738	746	
34	754	762	770	779	787	795	803	811	819	827	
35	835	843	852	860	868	876	884	892	900	908	
36	916	925	933	941	949	957	965	973	981	989	
37	72 997	*006	*014	*022	*030	*038	*046	*054	*062	*070	
38	73 078	086	094	102	111	119	127	135	143	151	
39	159	167	175	183	191	199	207	215	223	231	
540	239	247	255	263	272	280	288	296	304	312	
41	320	328	336	344	352	360	368	376	384	392	
42	400	408	416	424	432	440	448	456	464	472	
43	480	488	496	504	512	520	528	536	544	552	
44	560	568	576	584	592	600	608	616	624	632	
45	640	648	656	664	672	679	687	695	703	711	
46	719	727	735	743	751	759	767	775	783	791	
47	799	807	815	823	830	838	846	854	862	870	
48	878	886	894	902	910	918	926	933	941	949	
49	73 957	965	973	981	989	997	*005	*013	*020	*028	
550	74 036	044	052	060	068	076	084	092	099	107	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

9	
1	0.9
2	1.8
3	2.7
4	3.6
5	4.5
6	5.4
7	6.3
8	7.2
9	8.1

8	
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

7	
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		550	74 036	044	052	060	068	076	084	092	099	107
		51	115	123	131	139	147	155	162	170	178	186
		52	194	202	210	218	225	233	241	249	257	265
		53	273	280	288	296	304	312	320	327	335	343
		54	351	359	367	374	382	390	398	406	414	421
		55	429	437	445	453	461	468	476	484	492	500
		56	507	515	523	531	539	547	554	562	570	578
		57	586	593	601	609	617	624	632	640	648	656
		58	663	671	679	687	695	702	710	718	726	733
		59	741	749	757	764	772	780	788	796	803	811
		560	819	827	834	842	850	858	865	873	881	889
		61	896	904	912	920	927	935	943	950	958	966
		62	74 974	981	989	997	*005	*012	*020	*028	*035	*043
		63	75 051	059	066	074	082	089	097	105	113	120
		64	128	136	143	151	159	166	174	182	189	197
		65	205	213	220	228	236	243	251	259	266	274
		66	282	289	297	305	312	320	328	335	343	351
		67	358	366	374	381	389	397	404	412	420	427
		68	435	442	450	458	465	473	481	488	496	504
		69	511	519	526	534	542	549	557	565	572	580
		570	587	595	603	610	618	626	633	641	648	656
		71	664	671	679	686	694	702	709	717	724	732
		72	740	747	755	762	770	778	785	793	800	808
		73	815	823	831	838	846	853	861	868	876	884
		74	891	899	906	914	921	929	937	944	952	959
		75	75 967	974	982	989	997	*005	*012	*020	*027	*035
		76	76 042	050	057	065	072	080	087	095	103	110
		77	118	125	133	140	148	155	163	170	178	185
		78	193	200	208	215	223	230	238	245	253	260
		79	268	275	283	290	298	305	313	320	328	335
		580	343	350	358	365	373	380	388	395	403	410
		81	418	425	433	440	448	455	462	470	477	485
		82	492	500	507	515	522	530	537	545	552	559
		83	567	574	582	589	597	604	612	619	626	634
		84	641	649	656	664	671	678	686	693	701	708
		85	716	723	730	738	745	753	760	768	775	782
		86	790	797	805	812	819	827	834	842	849	856
		87	864	871	879	886	893	901	908	916	923	930
		88	76 938	945	953	960	967	975	982	989	997	*004
		89	77 012	019	026	034	041	048	056	063	070	078
		590	085	093	100	107	115	122	129	137	144	151
		91	159	166	173	181	188	195	203	210	217	225
		92	232	240	247	254	262	269	276	283	291	298
		93	305	313	320	327	335	342	349	357	364	371
		94	379	386	393	401	408	415	422	430	437	444
		95	452	459	466	474	481	488	495	503	510	517
		96	525	532	539	546	554	561	568	576	583	590
		97	597	605	612	619	627	634	641	648	656	663
		98	670	677	685	692	699	706	714	721	728	735
		99	743	750	757	764	772	779	786	793	801	808
		600	77 815	822	830	837	844	851	859	866	873	880
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9

8	
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

7	
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
600	77 815	822	830	837	844	851	859	866	873	880	
01	887	895	902	909	916	924	931	938	945	952	
02	77 960	967	974	981	988	996	*003	*010	*017	*025	
03	78 032	039	046	053	061	068	075	082	089	097	
04	104	111	118	125	132	140	147	154	161	168	
05	176	183	190	197	204	211	219	226	233	240	
06	247	254	262	269	276	283	290	297	305	312	
07	319	326	333	340	347	355	362	369	376	383	
08	390	398	405	412	419	426	433	440	447	455	
09	462	469	476	483	490	497	504	512	519	526	
610	533	540	547	554	561	569	576	583	590	597	
11	604	611	618	625	633	640	647	654	661	668	
12	675	682	689	696	704	711	718	725	732	739	
13	746	753	760	767	774	781	789	796	803	810	
14	817	824	831	838	845	852	859	866	873	880	
15	888	895	902	909	916	923	930	937	944	951	
16	78 958	965	972	979	986	993	*000	*007	*014	*021	
17	79 029	036	043	050	057	064	071	078	085	092	
18	099	106	113	120	127	134	141	148	155	162	
19	169	176	183	190	197	204	211	218	225	232	
620	239	246	253	260	267	274	281	288	295	302	
21	309	316	323	330	337	344	351	358	365	372	
22	379	386	393	400	407	414	421	428	435	442	
23	449	456	463	470	477	484	491	498	505	511	
24	518	525	532	539	546	553	560	567	574	581	
25	588	595	602	609	616	623	630	637	644	650	
26	657	664	671	678	685	692	699	706	713	720	
27	727	734	741	748	754	761	768	775	782	789	
28	796	803	810	817	824	831	837	844	851	858	
29	865	872	879	886	893	900	906	913	920	927	
630	79 934	941	948	955	962	969	975	982	989	996	
31	80 003	010	017	024	030	037	044	051	058	065	
32	072	079	085	092	099	106	113	120	127	134	
33	140	147	154	161	168	175	182	188	195	202	
34	209	216	223	229	236	243	250	257	264	271	
35	277	284	291	298	305	312	318	325	332	339	
36	346	353	359	366	373	380	387	393	400	407	
37	414	421	428	434	441	448	455	462	468	475	
38	482	489	496	502	509	516	523	530	536	543	
39	550	557	564	570	577	584	591	598	604	611	
640	618	625	632	638	645	652	659	665	672	679	
41	686	693	699	706	713	720	726	733	740	747	
42	754	760	767	774	781	787	794	801	808	814	
43	821	828	835	841	848	855	862	868	875	882	
44	889	895	902	909	916	922	929	936	943	949	
45	80 956	963	969	976	983	990	996	*003	*010	*017	
46	81 023	030	037	043	050	057	064	070	077	084	
47	090	097	104	111	117	124	131	137	144	151	
48	158	164	171	178	184	191	198	204	211	218	
49	224	231	238	245	251	258	265	271	278	285	
650	81 291	298	305	311	318	325	331	338	345	351	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

8  
1 0.8  
2 1.6  
3 2.4  
4 3.2  
5 4.0  
6 4.8  
7 5.6  
8 6.4  
9 7.2

7  
1 0.7  
2 1.4  
3 2.1  
4 2.8  
5 3.5  
6 4.2  
7 4.9  
8 5.6  
9 6.3

6  
1 0.6  
2 1.2  
3 1.8  
4 2.4  
5 3.0  
6 3.6  
7 4.2  
8 4.8  
9 5.4

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		650	81 291	298	305	311	318	325	331	338	345	351
		51	358	365	371	378	385	391	398	405	411	418
		52	425	431	438	445	451	458	465	471	478	485
		53	491	498	505	511	518	525	531	538	544	551
		54	558	564	571	578	584	591	598	604	611	617
		55	624	631	637	644	651	657	664	671	677	684
		56	690	697	704	710	717	723	730	737	743	750
		57	757	763	770	776	783	790	796	803	809	816
		58	823	829	836	842	849	856	862	869	875	882
		59	889	895	902	908	915	921	928	935	941	948
		660	81 954	961	968	974	981	987	994	*000	*007	*014
		61	82 020	027	033	040	046	053	060	066	073	079
		62	086	092	099	105	112	119	125	132	138	145
		63	151	158	164	171	178	184	191	197	204	210
		64	217	223	230	236	243	249	256	263	269	276
		65	282	289	295	302	308	315	321	328	334	341
		66	347	354	360	367	373	380	387	393	400	406
		67	413	419	426	432	439	445	452	458	465	471
		68	478	484	491	497	504	510	517	523	530	536
		69	543	549	556	562	569	575	582	588	595	601
		670	607	614	620	627	633	640	646	653	659	666
		71	672	679	685	692	698	705	711	718	724	730
		72	737	743	750	756	763	769	776	782	789	795
		73	802	808	814	821	827	834	840	847	853	860
		74	866	872	879	885	892	898	905	911	918	924
		75	930	937	943	950	956	963	969	975	982	988
		76	82 995	*001	*008	*014	*020	*027	*033	*040	*046	*052
		77	83 059	065	072	078	085	091	097	104	110	117
		78	123	129	136	142	149	155	161	168	174	181
		79	187	193	200	206	213	219	225	232	238	245
		680	251	257	264	270	276	283	289	296	302	308
		81	315	321	327	334	340	347	353	359	366	372
		82	378	385	391	398	404	410	417	423	429	436
		83	442	448	455	461	467	474	480	487	493	499
		84	506	512	518	525	531	537	544	550	556	563
		85	569	575	582	588	594	601	607	613	620	626
		86	632	639	645	651	658	664	670	677	683	689
		87	696	702	708	715	721	727	734	740	746	753
		88	759	765	771	778	784	790	797	803	809	816
		89	822	828	835	841	847	853	860	866	872	879
		690	885	891	897	904	910	916	923	929	935	942
		91	83 948	954	960	967	973	979	985	992	998	*004
		92	84 011	017	023	029	036	042	048	055	061	067
		93	073	080	086	092	098	105	111	117	123	130
		94	136	142	148	155	161	167	173	180	186	192
		95	198	205	211	217	223	230	236	242	248	255
		96	261	267	273	280	286	292	298	305	311	317
		97	323	330	336	342	348	354	361	367	373	379
		98	386	392	398	404	410	417	423	429	435	442
		99	448	454	460	466	473	479	485	491	497	504
		700	84 510	516	522	528	535	541	547	553	559	566
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
700	84 510	516	522	528	535	541	547	553	559	566	
01	572	578	584	590	597	603	609	615	621	628	
02	634	640	646	652	658	665	671	677	683	689	
03	696	702	708	714	720	726	733	739	745	751	
04	757	763	770	776	782	788	794	800	807	813	
05	819	825	831	837	844	850	856	862	868	874	
06	880	887	893	899	905	911	917	924	930	936	
07	84 942	948	954	960	967	973	979	985	991	997	
08	85 003	009	016	022	028	034	040	046	052	058	
09	065	071	077	083	089	095	101	107	114	120	
710	126	132	138	144	150	156	163	169	175	181	
11	187	193	199	205	211	217	224	230	236	242	
12	248	254	260	266	272	278	285	291	297	303	
13	309	315	321	327	333	339	345	352	358	364	
14	370	376	382	388	394	400	406	412	418	425	
15	431	437	443	449	455	461	467	473	479	485	
16	491	497	503	509	516	522	528	534	540	546	
17	552	558	564	570	576	582	588	594	600	606	
18	612	618	625	631	637	643	649	655	661	667	
19	673	679	685	691	697	703	709	715	721	727	
720	733	739	745	751	757	763	769	775	781	788	
21	794	800	806	812	818	824	830	836	842	848	
22	854	860	866	872	878	884	890	896	902	908	
23	914	920	926	932	938	944	950	956	962	968	
24	85 974	980	986	992	998	*004	*010	*016	*022	*028	
25	86 034	040	046	052	058	064	070	076	082	088	
26	094	100	106	112	118	124	130	136	141	147	
27	153	159	165	171	177	183	189	195	201	207	
28	213	219	225	231	237	243	249	255	261	267	
29	273	279	285	291	297	303	308	314	320	326	
730	332	338	344	350	356	362	368	374	380	386	
31	392	398	404	410	415	421	427	433	439	445	
32	451	457	463	469	475	481	487	493	499	504	
33	510	516	522	528	534	540	546	552	558	564	
34	570	576	581	587	593	599	605	611	617	623	
35	629	635	641	646	652	658	664	670	676	682	
36	688	694	700	705	711	717	723	729	735	741	
37	747	753	759	764	770	776	782	788	794	800	
38	806	812	817	823	829	835	841	847	853	859	
39	864	870	876	882	888	894	900	906	911	917	
740	923	929	935	941	947	953	958	964	970	976	
41	86 982	988	994	999	*005	*011	*017	*023	*029	*035	
42	87 040	046	052	058	064	070	075	081	087	093	
43	099	105	111	116	122	128	134	140	146	151	
44	157	163	169	175	181	186	192	198	204	210	
45	216	221	227	233	239	245	251	256	262	268	
46	274	280	286	291	297	303	309	315	320	326	
47	332	338	344	349	355	361	367	373	379	384	
48	390	396	402	408	413	419	425	431	437	442	
49	448	454	460	466	471	477	483	489	495	500	
750	87 506	512	518	523	529	535	541	547	552	558	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

7	
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

6	
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

5	
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		750	87 506	512	518	523	529	535	541	547	552	558
		51	564	570	576	581	587	593	599	604	610	616
		52	622	628	633	639	645	651	656	662	668	674
		53	679	685	691	697	703	708	714	720	726	731
		54	737	743	749	754	760	766	772	777	783	789
		55	795	800	806	812	818	823	829	835	841	846
		56	852	858	864	869	875	881	887	892	898	904
		57	910	915	921	927	933	938	944	950	955	961
		58	87 967	973	978	984	990	996	*001	*007	*013	*018
		59	88 024	030	036	041	047	053	058	064	070	076
		760	081	087	093	098	104	110	116	121	127	133
		61	138	144	150	156	161	167	173	178	184	190
		62	195	201	207	213	218	224	230	235	241	247
		63	252	258	264	270	275	281	287	292	298	304
		64	309	315	321	326	332	338	343	349	355	360
		65	366	372	377	383	389	395	400	406	412	417
		66	423	429	434	440	446	451	457	463	468	474
		67	480	485	491	497	502	508	513	519	525	530
		68	536	542	547	553	559	564	570	576	581	587
		69	593	598	604	610	615	621	627	632	638	643
		770	649	655	660	666	672	677	683	689	694	700
		71	705	711	717	722	728	734	739	745	750	756
		72	762	767	773	779	784	790	795	801	807	812
		73	818	824	829	835	840	846	852	857	863	868
		74	874	880	885	891	897	902	908	913	919	925
		75	930	936	941	947	953	958	964	969	975	981
		76	88 986	992	997	*003	*009	*014	*020	*025	*031	*037
		77	89 042	048	053	059	064	070	076	081	087	092
		78	098	104	109	115	120	126	131	137	143	148
		79	154	159	165	170	176	182	187	193	198	204
		780	209	215	221	226	232	237	243	248	254	260
		81	265	271	276	282	287	293	298	304	310	315
		82	321	326	332	337	343	348	354	360	365	371
		83	376	382	387	393	398	404	409	415	421	426
		84	432	437	443	448	454	459	465	470	476	481
		85	487	492	498	504	509	515	520	526	531	537
		86	542	548	553	559	564	570	575	581	586	592
		87	597	603	609	614	620	625	631	636	642	647
		88	653	658	664	669	675	680	686	691	697	702
		89	708	713	719	724	730	735	741	746	752	757
		790	763	768	774	779	785	790	796	801	807	812
		91	818	823	829	834	840	845	851	856	862	867
		92	873	878	883	889	894	900	905	911	916	922
		93	927	933	938	944	949	955	960	966	971	977
		94	89 982	988	993	998	*004	*009	*015	*020	*026	*031
		95	90 037	042	048	053	059	064	069	075	080	086
		96	091	097	102	108	113	119	124	129	135	140
		97	146	151	157	162	168	173	179	184	189	195
		98	200	206	211	217	222	227	233	238	244	249
		99	255	260	266	271	276	282	287	293	298	304
		800	90 309	314	320	325	331	336	342	347	352	358
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9

1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
800	90 309	314	320	325	331	336	342	347	352	358	
01	363	369	374	380	385	390	396	401	407	412	
02	417	423	428	434	439	445	450	455	461	466	
03	472	477	482	488	493	499	504	509	515	520	
04	526	531	536	542	547	553	558	563	569	574	
05	580	585	590	596	601	607	612	617	623	628	
06	634	639	644	650	655	660	666	671	677	682	
07	687	693	698	703	709	714	720	725	730	736	
08	741	747	752	757	763	768	773	779	784	789	
09	795	800	806	811	816	822	827	832	838	843	
810	849	854	859	865	870	875	881	886	891	897	
11	902	907	913	918	924	929	934	940	945	950	
12	90 956	961	966	972	977	982	988	993	998	*004	
13	91 009	014	020	025	030	036	041	046	052	057	
14	062	068	073	078	084	089	094	100	105	110	
15	116	121	126	132	137	142	148	153	158	164	
16	169	174	180	185	190	196	201	206	212	217	
17	222	228	233	238	243	249	254	259	265	270	
18	275	281	286	291	297	302	307	312	318	323	
19	328	334	339	344	350	355	360	365	371	376	
820	381	387	392	397	403	408	413	418	424	429	
21	434	440	445	450	455	461	466	471	477	482	
22	487	492	498	503	508	514	519	524	529	535	
23	540	545	551	556	561	566	572	577	582	587	
24	593	598	603	609	614	619	624	630	635	640	
25	645	651	656	661	666	672	677	682	687	693	
26	698	703	709	714	719	724	730	735	740	745	
27	751	756	761	766	772	777	782	787	793	798	
28	803	808	814	819	824	829	834	840	845	850	
29	855	861	866	871	876	882	887	892	897	903	
830	908	913	918	924	929	934	939	944	950	955	
31	91 960	965	971	976	981	986	991	997	*002	*007	
32	92 012	018	023	028	033	038	044	049	054	059	
33	065	070	075	080	085	091	096	101	106	111	
34	117	122	127	132	137	143	148	153	158	163	
35	169	174	179	184	189	195	200	205	210	215	
36	221	226	231	236	241	247	252	257	262	267	
37	273	278	283	288	293	298	304	309	314	319	
38	324	330	335	340	345	350	355	361	366	371	
39	376	381	387	392	397	402	407	412	418	423	
840	428	433	438	443	449	454	459	464	469	474	
41	480	485	490	495	500	505	511	516	521	526	
42	531	536	542	547	552	557	562	567	572	578	
43	583	588	593	598	603	609	614	619	624	629	
44	634	639	645	650	655	660	665	670	675	681	
45	686	691	696	701	706	711	716	722	727	732	
46	737	742	747	752	758	763	768	773	778	783	
47	788	793	799	804	809	814	819	824	829	834	
48	840	845	850	855	860	865	870	875	881	886	
49	891	896	901	906	911	916	921	927	932	937	
850	92 942	947	952	957	962	967	973	978	983	988	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

6

1 0.6  
2 1.2  
3 1.8  
4 2.4  
5 3.0  
6 3.6  
7 4.2  
8 4.8  
9 5.4

5

1 0.5  
2 1.0  
3 1.5  
4 2.0  
5 2.5  
6 3.0  
7 3.5  
8 4.0  
9 4.5

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		850	92 942	947	952	957	962	967	973	978	983	988
		51	92 993	998	*003	*008	*013	*018	*024	*029	*034	*039
		52	93 044	049	054	059	064	069	075	080	085	090
		53	095	100	105	110	115	120	125	131	136	141
		54	146	151	156	161	166	171	176	181	186	192
		55	197	202	207	212	217	222	227	232	237	242
		56	247	252	258	263	268	273	278	283	288	293
		57	298	303	308	313	318	323	328	334	339	344
		58	349	354	359	364	369	374	379	384	389	394
		59	399	404	409	414	420	425	430	435	440	445
		860	450	455	460	465	470	475	480	485	490	495
		61	500	505	510	515	520	526	531	536	541	546
		62	551	556	561	566	571	576	581	586	591	596
		63	601	606	611	616	621	626	631	636	641	646
		64	651	656	661	666	671	676	682	687	692	697
		65	702	707	712	717	722	727	732	737	742	747
		66	752	757	762	767	772	777	782	787	792	797
		67	802	807	812	817	822	827	832	837	842	847
		68	852	857	862	867	872	877	882	887	892	897
		69	902	907	912	917	922	927	932	937	942	947
		870	93 952	957	962	967	972	977	982	987	992	997
		71	94 002	007	012	017	022	027	032	037	042	047
		72	052	057	062	067	072	077	082	086	091	096
		73	101	106	111	116	121	126	131	136	141	146
		74	151	156	161	166	171	176	181	186	191	196
		75	201	206	211	216	221	226	231	236	240	245
		76	250	255	260	265	270	275	280	285	290	295
		77	300	305	310	315	320	325	330	335	340	345
		78	349	354	359	364	369	374	379	384	389	394
		79	399	404	409	414	419	424	429	433	438	443
		880	448	453	458	463	468	473	478	483	488	493
		81	498	503	507	512	517	522	527	532	537	542
		82	547	552	557	562	567	571	576	581	586	591
		83	596	601	606	611	616	621	626	630	635	640
		84	645	650	655	660	665	670	675	680	685	689
		85	694	699	704	709	714	719	724	729	734	738
		86	743	748	753	758	763	768	773	778	783	787
		87	792	797	802	807	812	817	822	827	832	836
		88	841	846	851	856	861	866	871	876	880	885
		89	890	895	900	905	910	915	919	924	929	934
		890	939	944	949	954	959	963	968	973	978	983
		91	94 988	993	998	*002	*007	*012	*017	*022	*027	*032
		92	95 036	041	046	051	056	061	066	071	075	080
		93	085	090	095	100	105	109	114	119	124	129
		94	134	139	143	148	153	158	163	168	173	177
		95	182	187	192	197	202	207	211	216	221	226
		96	231	236	240	245	250	255	260	265	270	274
		97	279	284	289	294	299	303	308	313	318	323
		98	328	332	337	342	347	352	357	361	366	371
		99	376	381	386	390	395	400	405	410	415	419
		900	95 424	429	434	439	444	448	453	458	463	468
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9

1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

1	0.4
2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6



N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
900	95 424	429	434	439	444	448	453	458	463	468	
01	472	477	482	487	492	497	501	506	511	516	
02	521	525	530	535	540	545	550	554	559	564	
03	569	574	578	583	588	593	598	602	607	612	
04	617	622	626	631	636	641	646	650	655	660	
05	665	670	674	679	684	689	694	698	703	708	
06	713	718	722	727	732	737	742	746	751	756	
07	761	766	770	775	780	785	789	794	799	804	
08	809	813	818	823	828	832	837	842	847	852	
09	856	861	866	871	875	880	885	890	895	899	
910	904	909	914	918	923	928	933	938	942	947	
11	952	957	961	966	971	976	980	985	990	995	
12	95 999	*004	*009	*014	*019	*023	*028	*033	*038	*042	
13	96 047	052	057	061	066	071	076	080	085	090	
14	095	099	104	109	114	118	123	128	133	137	
15	142	147	152	156	161	166	171	175	180	185	
16	190	194	199	204	209	213	218	223	227	232	
17	237	242	246	251	256	261	265	270	275	280	
18	284	289	294	298	303	308	313	317	322	327	
19	332	336	341	346	350	355	360	365	369	374	
920	379	384	388	393	398	402	407	412	417	421	
21	426	431	435	440	445	450	454	459	464	468	
22	473	478	483	487	492	497	501	506	511	515	
23	520	525	530	534	539	544	548	553	558	562	
24	567	572	577	581	586	591	595	600	605	609	
25	614	619	624	628	633	638	642	647	652	656	
26	661	666	670	675	680	685	689	694	699	703	
27	708	713	717	722	727	731	736	741	745	750	
28	755	759	764	769	774	778	783	788	792	797	
29	802	806	811	816	820	825	830	834	839	844	
930	848	853	858	862	867	872	876	881	886	890	
31	895	900	904	909	914	918	923	928	932	937	
32	942	946	951	956	960	965	970	974	979	984	
33	96 988	993	997	*002	*007	*011	*016	*021	*025	*030	
34	97 035	039	044	049	053	058	063	067	072	077	
35	081	086	090	095	100	104	109	114	118	123	
36	128	132	137	142	146	151	155	160	165	169	
37	174	179	183	188	192	197	202	206	211	216	
38	220	225	230	234	239	243	248	253	257	262	
39	267	271	276	280	285	290	294	299	304	308	
940	313	317	322	327	331	336	340	345	350	354	
41	359	364	368	373	377	382	387	391	396	400	
42	405	410	414	419	424	428	433	437	442	447	
43	451	456	460	465	470	474	479	483	488	493	
44	497	502	506	511	516	520	525	529	534	539	
45	543	548	552	557	562	566	571	575	580	585	
46	589	594	598	603	607	612	617	621	626	630	
47	635	640	644	649	653	658	663	667	672	676	
48	681	685	690	695	699	704	708	713	717	722	
49	727	731	736	740	745	749	754	759	763	768	
950	97 772	777	782	786	791	795	800	804	809	813	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

1	5
2	0.5
3	1.0
4	1.5
5	2.0
6	2.5
7	3.0
8	3.5
9	4.0
	4.5

1	4
2	0.4
3	0.8
4	1.2
5	1.6
6	2.0
7	2.4
8	2.8
9	3.2
	3.6

Prop. Parts		N	0	1	2	3	4	5	6	7	8	9
		950	97 772	777	782	786	791	795	800	804	809	813
		51	818	823	827	832	836	841	845	850	855	859
		52	864	868	873	877	882	886	891	896	900	905
		53	909	914	918	923	928	932	937	941	946	950
		54	97 955	959	964	968	973	978	982	987	991	996
		55	98 000	005	009	014	019	023	028	032	037	041
		56	046	050	055	059	064	068	073	078	082	087
		57	091	096	100	105	109	114	118	123	127	132
		58	137	141	146	150	155	159	164	168	173	177
		59	182	186	191	195	200	204	209	214	218	223
		960	227	232	236	241	245	250	254	259	263	268
		61	272	277	281	286	290	295	299	304	308	313
		62	318	322	327	331	336	340	345	349	354	358
		63	363	367	372	376	381	385	390	394	399	403
		64	408	412	417	421	426	430	435	439	444	448
		65	453	457	462	466	471	475	480	484	489	493
		66	498	502	507	511	516	520	525	529	534	538
		67	543	547	552	556	561	565	570	574	579	583
		68	588	592	597	601	605	610	614	619	623	628
		69	632	637	641	646	650	655	659	664	668	673
		970	677	682	686	691	695	700	704	709	713	717
		71	722	726	731	735	740	744	749	753	758	762
		72	767	771	776	780	784	789	793	798	802	807
		73	811	816	820	825	829	834	838	843	847	851
		74	856	860	865	869	874	878	883	887	892	896
		75	900	905	909	914	918	923	927	932	936	941
		76	945	949	954	958	963	967	972	976	981	985
		77	98 989	994	998	*003	*007	*012	*016	*021	*025	*029
		78	99 034	038	043	047	052	056	061	065	069	074
		79	078	083	087	092	096	100	105	109	114	118
		980	123	127	131	136	140	145	149	154	158	162
		81	167	171	176	180	185	189	193	198	202	207
		82	211	216	220	224	229	233	238	242	247	251
		83	255	260	264	269	273	277	282	286	291	295
		84	300	304	308	313	317	322	326	330	335	339
		85	344	348	352	357	361	366	370	374	379	383
		86	388	392	396	401	405	410	414	419	423	427
		87	432	436	441	445	449	454	458	463	467	471
		88	476	480	484	489	493	498	502	506	511	515
		89	520	524	528	533	537	542	546	550	555	559
		990	564	568	572	577	581	585	590	594	599	603
		91	607	612	616	621	625	629	634	638	642	647
		92	651	656	660	664	669	673	677	682	686	691
		93	695	699	704	708	712	717	721	726	730	734
		94	739	743	747	752	756	760	765	769	774	778
		95	782	787	791	795	800	804	808	813	817	822
		96	826	830	835	839	843	848	852	856	861	865
		97	870	874	878	883	887	891	896	900	904	909
		98	913	917	922	926	930	935	939	944	948	952
		99	99 957	961	965	970	974	978	983	987	991	996
		1000	00 000	004	009	013	017	022	026	030	035	039
Prop. Parts		N	0	1	2	3	4	5	6	7	8	9

1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

1	0.4
2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6





## INDEX

### A

- Accuracy, 12
- Acidity, determination of, 49
- Acids, 48
  - degree of ionization, 64, 65
  - standard solution of, 53
  - table of concentration, 248
- Alkalinity, determination of, 49
- Analysis, indirect, 228
  - proximate, 213
  - systematic, 213
  - ultimate, 213
  - volumetric, 29
- Arsenic, determination of, 144
- Arsenite, standard solution of, 149
- Atomic weights, calculation of, 236
  - table of, inside back cover

### B

- Balance, exercises with, 46
  - use of, 18
- Balancing equations, 103
- Base, standardization of, 56
- Brass, analysis of, 222
- Bromate methods, 155
- Buffer solutions, 186
- Buoyancy, correction for, 22
- Buret, calibration of, 35

### C

- Calcium, gravimetric determination of, 201
  - volumetric determination of, 135
- Calculations of:
  - atomic weights, 236
  - dichromate methods, 120
  - factor weight samples, 210
  - formulas, 234
  - gravimetric analysis, 174
  - indirect analysis, 228
  - iodometric methods, 157
  - ionic equilibria, 89
  - mixed alkalies, 93

### Calculations of: (*Continued*)

- mixed halides, 206
- neutralization methods, 59, 89, 97
- pH-permanganate methods, 140
- pH values, 62
- reagents, 23
- solubility product constants, 181
- volumetric analysis, 35
- volumetric precipitation, 167
- Calibration, of buret, 35
  - of flasks, 34
  - of weights, 21
- Ceric sulfate methods, 141
- Chemical Equilibrium, Law of, 6, 61, 107, 161, 181
- Chemical factors, 177
- Chlorides, determination of, 162, 191
- Cleaning solution, 45
- Combining weights, 9
- Common-ion effect, 184
- Complex ions, 166
- Computation rules, 13
- Concentration, hydrogen-ion, 63
- Copper, electrolytic determination of, 225
  - iodometric determination of, 151
- Current density, 225

### D

- Definite Composition, Law of, 8
- Density tables, of acids, 248
  - of ammonia, 250
  - of water, 250
- Desiccator, 48
- Determination of:
  - acidity of oxalic acid, 57
  - alkalinity of soda ash, 49
  - arsenic, 144
  - calcium, gravimetric, 201
    - volumetric, 135
  - carbon dioxide, 244
  - chlorides, 162, 191
  - copper, electrolytic, 226
    - iodometric, 151



Determination of: (*Continued*)

- hydrogen peroxide, 138
  - iron, by dichromate, 115
    - by permanganate, 126
    - gravimetrically, 195
  - lead, 226, 231
  - magnesium, 204
  - moisture, 217
  - normality, 38
  - oxalic acid, 57
  - phosphates, 206
  - potassium acid phthalate, 56
  - pyrolusite, 139
  - silica, 218
  - silver, 165
  - soda ash, 54
  - sulfates, 198
  - tin, 225
  - water of crystallization, 217
  - zinc, 227
- Dichromate methods, 115
  - calculations of, 120
- Dilution problems, 25

## E

- Electrochemical analysis, 222
- Electrode potentials, 106
- Electron transfer, 103
- End points, 32
- Equilibrium, Law of Chemical, 6, 61, 107, 161, 181
- Equivalent weight, 38, 104
- Errors of analysis, 11
- Evolution methods, 216
- Exponents, 14

## F

- Factor weight samples, 210
- Factors, chemical, 177
- Faraday's laws, 224
- Filtering, 173
- Formulas, calculation of, 234

## G

- Gooch crucible, preparation of, 192
- Gravimetric precipitation, 169
- Gravimetric procedures, 190

## H

- Half-cell reactions, 102
- Halides, calculations of mixed, 206
  - precipitation of, 190
- Hydrogen electrode, 88
- Hydrogen-ion concentration, 63
- Hydrolysis, 66
- Hydroxides, precipitation of, 194

## I

- Ignition of precipitates, 173
- Indicators, 31
  - chart, 84
  - list, 83
  - theory of, 83
- Iodate methods, 155
- Iodine, standard solution of, 146, 152
  - table, 64, 65
- Iodometric calculations, 148, 157
- Iron, dichromate determination of, 115
  - gravimetric determination of, 195
  - permanganate determination of, 126

## J

- Jones reductor, preparation and use, 132

## L

- Lead, determination of, 226, 231
- Limestone analysis, 219
- Liter, 33
- Literature, 241
- Logarithms, table of, 262-279
  - use of, 14

## M

- Magnesium, determination of, 204
- Methyl orange, structure, 87
- Milliequivalent, 38
- Mixed alkalis, calculation of, 93
- Moisture, determination of, 48, 217
- Molar potentials, 106

## N

- Nernst equation, 105
- Neutralization methods, 45



Normality, 38  
 calculation of, 39  
 Notebook, 2

## O

Overvoltage, 224  
 Oxalic acid, determination of, 57  
 Oxidation, electrochemical nature of, 104  
 Oxidizing agents, 102  
 table of, 108

## P

Permanganate methods, 122  
 calculation of, 140  
 uses of, 123  
 pH value, 62  
 of indicators, 83  
 table of values, 64, 70, 76  
 Phenolphthalein, 56, 87, 247  
 Phosphates, 203  
 determination of, 206  
 Plan of course, 243  
 Potentials, table of, 108  
 Potentiometric titration, 67, 87  
 Precipitates, ignition of, 173  
 washing of, 173  
 Precipitation, 169  
 electrolytic, 222  
 volumetric, 160  
 Precision, 11  
 Pyrophosphate, 205, 209

## R

Reactions, between acids and bases, 48, 68, 72  
 half-cell, 102  
 of oxidation, 113  
 Reagents, calculation of, 23  
 list of, 245  
 Redox indicators, 112  
 Reducing agents, 23  
 Report forms, 253, 255

## S

Sampling, 10  
 Significant figures, 13

Silica, determination of, 218  
 Silver, determination of, 165  
 Solubility product principle, 8, 47  
 table of solubility products, 181  
 use of, 186  
 Solutions, adjustment of, 91  
 buffer, 186  
 standard, 30  
 standardization of, *see* Standardization  
 Specific gravity, calculations involving, 195  
 tables, *see* Density tables  
 Standardization, 31  
 of solutions of:  
 ferrous salt, 119; 130, 134  
 hydrochloric acid, 52  
 iodine, 145  
 potassium dichromate, 118  
 potassium permanganate, 130, 134  
 potassium thiocyanate, 164  
 silver nitrate, 163  
 sodium arsenite, 145  
 sodium hydroxide, 56  
 sodium thiosulfate, 153  
 Stoichiometric calculations, 59  
 Sulfates, determination of, 198

## T

Tin, determination of, 225  
 Titration curves, 71, 75, 79  
 Titer, 37

## V

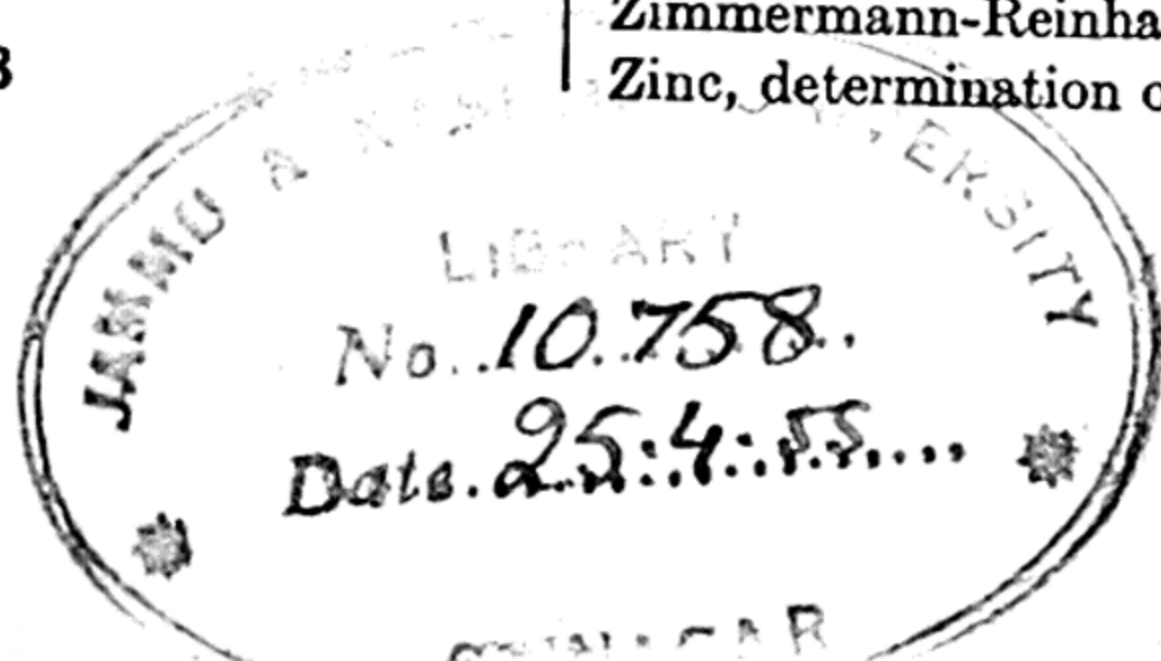
Valence, 99  
 balancing equations by, 103  
 Volumetric methods, calculations of, 35

## W

Water of crystallization, determination of, 217  
 Weights, calibration of, 21

## Z

Zimmermann-Reinhard method, 129  
 Zinc, determination of, 227





[illegible]

[illegible]



SECRET

SECRET

**SECRET**

100

\_\_\_\_\_

[illegible]

# INTERNATIONAL ATOMIC WEIGHTS

1943

Reprinted from the *Journal of the American Chemical Society*

	Sym- bol	Atomic Number	Atomic Weight		Sym- bol	Atomic Number	Atomic Weight
Aluminum...	Al	13	26.97	Molybdenum..	Mo	42	95.95
Antimony....	Sb	51	121.76	Neodymium..	Nd	60	144.27
Argon.....	A	18	39.944	Neon.....	Ne	10	20.183
Arsenic.....	As	33	74.91	Nickel.....	Ni	28	58.69
Barium.....	Ba	56	137.36	Nitrogen.....	N	7	14.008
Beryllium....	Be	4	9.02	Osmium.....	Os	76	190.2
Bismuth.....	Bi	83	209.00	Oxygen.....	O	8	16.0000
Boron.....	B	5	10.82	Palladium....	Pd	46	106.7
Bromine.....	Br	35	79.916	Phosphorus...	P	15	30.98
Cadmium.....	Cd	48	112.41	Platinum.....	Pt	78	195.23
Calcium.....	Ca	20	40.08	Potassium....	K	19	39.096
Carbon.....	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium.....	Ce	58	140.13	Protactinium..	Pa	91	231
Cesium.....	Cs	55	132.91	Radium.....	Ra	88	226.05
Chlorine.....	Cl	17	35.457	Radon.....	Rn	86	222
Chromium....	Cr	24	52.01	Rhenium.....	Re	75	186.31
Cobalt.....	Co	27	58.94	Rhodium.....	Rh	45	102.91
Columbium..	Cb	41	92.91	Rubidium....	Rb	37	85.48
Copper.....	Cu	29	63.57	Ruthenium...	Ru	44	101.7
Dysprosium..	Dy	66	162.46	Samarium....	Sm	62	150.43
Erbium.....	Er	68	167.2	Scandium....	Sc	21	45.10
Europium....	Eu	63	152.0	Selenium.....	Se	34	78.96
Fluorine.....	F	9	19.00	Silicon.....	Si	14	28.06
Gadolinium..	Gd	64	156.9	Silver.....	Ag	47	107.880
Gallium.....	Ga	31	69.72	Sodium.....	Na	11	22.997
Germanium..	Ge	32	72.60	Strontium....	Sr	38	87
Gold.....	Au	79	197.2	Sulfur.....	S	16	32
Hafnium.....	Hf	72	178.6	Tantalum....	Ta	73	180.948
Helium.....	He	2	4.003	Tellurium....	Te	52	127.60
Holmium....	Ho	67	164.94	Terbium.....	Tb	65	158.925
Hydrogen....	H	1	1.0080	Thallium....	Tl	81	204.38
Indium.....	In	49	114.76	Thorium.....	Th	90	232
Iodine.....	I	53	126.92	Thulium.....	Tm	69	168.930
Iridium.....	Ir	77	193.1	Tin.....	Sn	50	118.710
Iron.....	Fe	26	55.85	Titanium....	Ti	22	47.88
Krypton.....	Kr	36	83.7	Tungsten....	W	74	183.84
Lanthanum..	La	57	138.92	Uranium.....	U	92	238.029
Lead.....	Pb	82	207.21	Vanadium....	V	23	50.942
Lithium.....	Li	3	6.940	Xenon.....	Xe	54	131.29
Lutecium....	Lu	71	174.99				
Magnesium..	Mg	12	24.32				
Manganese...	Mn	25	54.93				
Mercury.....	Hg	80	200				

The Jammu & Kashmir  
University Library,  
Srinagar.

1. Overdue charge of one  
anna per-day will be  
charged for each volume  
kept after the due date.

2. Borrowers will be held  
responsible for any dam-  
age done to the book  
while in their possession.